Review Article

Potential Use of Industrial Cocoa Waste in Biofuel Production

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Worldwide, the wastes derived from food production are generated in elevated volumes annually. In particular, the cocoa industrial wastes represent a source of usable biomass for the elaboration of new products such as food, livestock feed, cosmetics, and chemical products, and they can even be used for the generation of biofuels. The cocoa industrial wastes include cocoa pod husk, mucilage, and bean shells, which contain compounds of interest for different industries. However, the lignocellulose content of these by-products requires a pretreatment to fully utilize them; thus, different biofuels can be produced, depending on the conversion technology used to obtain the highest biomass yield. Recent studies reported the use of cocoa industrial wastes for the production of solid, liquid, and gaseous biofuels; nevertheless, the most common use reported is as a direct combustion source, which is used to supply the same production plants. Therefore, the objective of this work is to carry out a review on the uses of the by-products generated from cocoa for the generation of biofuels, as well as the technological concept applied for the transformation. In addition, the future trends indicate the relevance of using catalysts in production to increase reactions in the conversion of compounds, including the use of statistical models to optimize the processing variables.

1. Introduction

The wastes resulting from the agriculture industry represent 50% of the fresh weight of the total harvested production; in energy terms, this is equivalent to the potential of 90 million tons of oil [1]. In addition, the growing world population demands a greater amount of energy; thus, the shortage of nonrenewable resources is imminent. In addition, the generation of industrial wastes and pollutants represents an ecological and socioeconomic challenge for the population [2]. Therefore, the use of wastes is essential to reduce the environmental impact and create an economic model based on the production of biocomposites [3].

In order to face this environmental problem, the application of the biorefinery concept is a promissory strategy; a biorefinery is defined as the sustainable synergistic processing of biomass on marketable food ingredients, products, and energy [4]. To carry out this process, it is necessary to guarantee the availability of wastes over time, the technical and economic capacity of their production, and the environmental impact produced during the generation cycle [5]. In this sense, residual biomass sources from industrial processing with the potential for the production of biofuels are explored.

In particular, cocoa (*Theobroma cacao* L.) is an umbrophilic crop of great importance in the world due to its applications in the food, cosmetic, and pharmaceutical industries. Cocoa is a tree native to Central and South America; however, the highest production is concentrated in areas with a tropical climate in Africa, Asia, and South America [6–8]. In 2017, the world production of cocoa pods was estimated at 4.2 million tons [9]. Meanwhile, cocoa industrial wastes were estimated at approximately 85% of world cocoa production; these wastes are cocoa pod husk (CPH), mucilage (CM), and bean shell (CBS) [10]. For the cocoa-producing industry, these wastes are a serious problem as they represent economic losses and environmental pollution [6]. In Figure 1, the wastes obtained from the cocoa fruit are shown.
The whole cocoa pod is a rich source of chemical compounds; however, the beans (main raw material) are the source with the highest content of fat, phenolic compounds, and alkaloids such as theobromine and caffeine [11]. Nevertheless, when the wastes are discarded in the first instance without treatment, they preserve different compounds that can be used to obtain other products through the biorefinery processing scheme [5].

Cocoa wastes contain lignocellulose, which can be used for the production of biofuels; however, it is necessary to carry out a pretreatment to degrade the structure and the fermentable compounds that can be used in a higher proportion. There are different types of pretreatments classified by their nature into chemical, physical, biological, and physicochemical; the choice of pretreatment will depend on the type of biomass and technical and economic aspects in the production of biofuel [12].

In order to reduce the generation of waste in agribusiness, the circular economy seeks options to transform these by-products into sources of bioactive compounds or for the generation of other products [13], as ingredients for food, livestock feed, or as a source for the development of biochemicals, biomaterials, and biofuels [14]. Table 1 shows the chemical composition of cocoa wastes.

The development of technologies that allow an adequate recovery of these wastes has become an economic advantage since it allows achieving the objective of zero waste in the cocoa industry [13].

The amount of cocoa wastes generated each year by the chocolate industry represents a severe health problem in the plantations, as well as an ecological damage, due to the amount of residual organic matter. Thus, the use of wastes is a contribution to minimizing the damage caused in an agroecosystem. Therefore, the objective of this work is to carry out a review on the use of the wastes generated from cocoa for the generation of biofuels, as well as the technological concept applied for the transformation.

### 2. Basic Concepts

Lignocellulose is an important part of plants; it is mainly found in herbs, trees, stems, husks, and flowers. The main source of lignocellulosic materials is residues from the forestry and agricultural industries. This material is of great importance due to its potential for energy production, which is derived from the composition of the heteromatrix, made up of cellulose, hemicellulose, and lignin that vary in quantity depending on the biomass of origin [24]. In Table 2, the lignocellulose composition of the cocoa wastes is shown.

Cellulose is the most abundant organic polymer in the world, and it is present in the cell wall of plant cells [30, 31]. However, the proportion depends on the type of biomass, and its range is between 30 and 60% [32]. Cellulose is a linear and crystalline structure formed by microfibers that are linked by hydrogen bonds [33]; this formation is due to the long chains of glucose with approximately 10,000 units, linked together by $\beta$-1,4-glucosidic bonds [34, 35].

On the other hand, a hemicellulose is a group of branched polysaccharides that connect cellulose with lignin [30]. Hemicellulose is made up of hexoses (glucose, galactose, and mannose) and pentoses (xylose and arabinose), along with other compounds in smaller quantities [34]. These compounds are linked by $\beta$-1,4-glucosidic and sometimes by $\beta$-1,3-glucosidic bonds [33]. The main differences between cellulose and hemicellulose are the degree of polymerization, the branching in the main chain in hemicellulose, and the weaker structure in the face of chemical agents [31]. The proportion of this material in the biomass ranges between 25 and 30% [36].

Finally, the lignin is a cross-linked aromatic phenolic polymer made up of phenylpropane units, responsible for the structural rigidity in the outer fibers in plants [30, 33]. This polymer is found in different proportions depending on its origin (softwood, hardwood, or agricultural residue), which can be between 10 and 35% [31]. The three main units that make up lignin are p-coumaryl, coniferyl, and sinapyl alcohol [34]. In Figure 2, the composition of lignocellulose with the structure and interaction of cellulose, hemicellulose, and lignin is shown.

### 3. Cocoa Industrial Wastes

#### 3.1. Cocoa Pod Husk

Cocoa pod husk (CPH) is the external part of the fruit; therefore, it is the main by-product generated from the processing of cocoa, and it represents 75% of the total weight [19]. For every ton of cocoa beans, an estimated 10 tons of wastes are generated, which are generally considered of none economic value [37]; this waste is generated after harvest, when pulping the fruit and recovering the grains covered by the mucilaginous layer [38].

CPH is made up of three layers, which are the endocarp, mesocarp, and epicarp; however, there are few specialized studies on the use of a part of the cocoa pod [39]. Normally, the most common use of the complete by-product is as fertilizer for the soil of the agroecosystem; nevertheless, there are phytosanitary problems such as pests and fungal diseases when using the CPH without treatment [19].

The chemical composition of CPH allows using this waste for different purposes. Biofuel production is possible using CPH, due to its lignocellulosic content [19]. Other compounds present in CPH are fiber, phenols, and minerals such as Ca, K, P, Mg, Na, Zn, Fe, Cu, and Mn [21, 40, 41].
3.2. Cocoa Mucilage. Cocoa mucilage (CM) is the whitish substance that covers the grain; other names as it is known are sweating or pulp [16]. The cocoa pulp juice is a fraction of CM, with a cloudy whitish appearance that is obtained after processing cocoa by means of handling and exerted pressure; this part of CM is widely used in obtaining products such as alcohol, vinegar, soft drinks, citric acid, and cocoa jelly [42].

The generation of CM is the result of the fruit pulping process; after splitting the cocoa pod in half, the beans are extracted with the mucilaginous layer. Immediately, they undergo a controlled fermentation where biochemical reactions are generated that allow the separation of the grain and the mucilage [43]. The amount of mucilage depends on the type of cocoa, maturation, and physical integrity of the fruits, which is reported between 3 and 5% of the total weight of cocoa [44].

CM is composed of spongy cells that contain cellular sap rich in different chemical compounds, containing 10–14% fermentable sugars (such as sucrose, glucose, and fructose), minerals (such as potassium, sodium, calcium, and magnesium), pectin, pentosans, citric acid, salts, cellulose, hemicellulose, and lignin [16, 42, 45].

3.3. Cocoa Bean Shell. Cocoa bean shell (CBS) is a lignocellulosic material obtained from the bean roasting process, and it constitutes 10–17% of the total weight of cocoa beans, although it may vary due to the fermentation process [18]. The importance of this waste lies in the migration of valuable compounds from the grain to the husk during fermentation [46]. The nutritional quality of CBS allows the generation of new products in the industry; in particular, the food, pharmaceutical, cosmetic, and agricultural industries have developed functional products based on this waste [47]. Moreover, CBS contains polysaccharides, phenolic compounds, methylxanthines [14], catechins, epicatechins, procyanidins, caffeine, theophylline, theobromine, and fiber [48–51]. Regarding energy, the potential content has been reported as an ecological source of alternative energy due to its calorific value, slightly higher than wood [6].

4. Biomass Conversion Technologies

The interest in the use of residual biomass from industrial processing has increased in the last decade since the quality of chemical compounds that conserve wastes can be used for the generation of new products with the application of different treatments [52]. The use of biomass in the production of biofuels is essential to reduce the consumption of fossil resources; this determines the development of an economy based on products of biological origin. For this reason, the type of biorefinery process will obtain the highest waste management in the agricultural industry [53].

The biorefinery can be classified by the system or model that is divided into seven categories, according to the type of biomass and technology used, which are conventional biorefinery, green, complete cultures, lignocellulosic raw material, the concept of two platforms, thermochemical, and marine [54]. The biorefinery is a process used for the
generation of different energy products with the application of different technologies for the transformation of biomass [55].

4.1. Physicochemical Conversion. Physicochemical conversion, also known as mechanical extraction, is used to produce liquid biofuels from the seeds of different foods [56]. The main sources used are sunflower and rapeseed; however, used cooking oil, animal fats, and seaweed oil are also used [57]. The oil can be subjected to an esterification or transesterification treatment to produce biodiesel, in which the intention is to transform the triglycerides present in the crude oil into fatty acids and glycerol [58]. In addition, solid waste is generated used for the manufacture of livestock feed [56].

4.2. Biological Conversion. Biological conversion involves microbial action for the decomposition of organic matter [59], and the objective is to produce liquid biofuels and biogas [57]. The most widely used microorganisms are yeasts; however, the use of fungal bacteria and specialized enzymes produces different products of value [58]. This type of technology is adaptable to different biomass sources; therefore, it is a widely used technique around the world [56]. The most relevant processes are fermentation and anaerobic digestion [59].

4.2.1. Anaerobic Digestion. Anaerobic digestion transforms the organic material into biogas, which consists of methane and carbon dioxide and small amounts of hydrogen sulfide [56]; the mechanism of action is activated in the presence of bacteria in a medium lacking oxygen [59]. This process is carried out in biomass with high moisture content (80–90%) [56]. A series of key actions in anaerobic digestion are identified where complex biomass compounds are first hydrolyzed into simpler compounds [57]. Then, acidogenesis occurs that transforms simple compounds into volatile fatty acids, H2, and CO2 [59]. Finally, methanogens convert organic acids into CH4 gas and CO2 [58].

4.2.2. Fermentation. Fermentation is an anaerobic biological process carried out by yeasts [56], where the goal is to convert sugars like glucose, fructose, and sucrose into ethanol and CO2 [59]. The sources most used in the generation of bioethanol are sugar cane and corn; however, in Europe, wheat and beet are used more frequently [56]. Biomass can be divided into three types: sugars, starch, and lignocellulosic materials [57].

The most common application is the action of yeasts for the fermentation of starch and generation of ethanol; nevertheless, the use of enzymes for the degradation of cellulose increases the production of ethanol [59]. Recent studies focus on the possibility of applying pretreatment to break the lignocellulosic structure of biomass of forest and agricultural origin for the production of ethanol by fermentation [56]. In addition, glycerol and carboxylic acids can be obtained as byproducts from this process. However, the quality and yield will depend on the type of biomass used and other process factors such as temperature, time, and pH [57]. The intention of the production of bioethanol is the gradual replacement of fuels of fossil origin; at present, mixtures of ethanol and gasoline are made (80–20%, respectively) [56]. On the other hand, solid waste after ethanol production can be used as boiler fuel or livestock feed [57]; generally, other treatments such as liquefaction, gasification, or pyrolysis can be used to produce other valuable products [58].

4.3. Thermochemical Conversion. Thermochemical conversion transforms the biomass by breaking bonds for the production of energy, biogas, and bio-oils [58]. The type of biomass must have low moisture content, but high values of organic matter [59]. In addition, the pyrolysis process is considered the basis of thermochemical treatments, due to the formation of solid, liquid, and gaseous residues that are generated [56].

The types of thermochemical treatments are combustion [59], gasification [56], pyrolysis [57], and liquefaction [60]. The choice of the type of treatment depends on different factors such as biomass quality and industry specifications, which include final application, environmental impact, and financial aspects [58]. Industrially, thermochemical processes are more efficient compared to biological processes, in relation to the reaction time and transformation of organic compounds [56].

4.3.1. Combustion. The combustion process is defined as the burning of fuel to release the energy contained in the form of heat of reaction [61]. In this context, combustion converts the chemical energy of biomass into thermal energy [59]; this process generates approximately 90% of the energy obtained through biomass [57]. Combustion transforms carbon into CO2, while hydrogen into H2O. Other compounds such as sulfur convert to SO2 and nitrogen to NOx [60].

Thermal degradation of biomass occurs in different steps [59]:

(i) Drying of biomass and release of highly volatile materials at a temperature between 25 and 125°C

(ii) Release and burning of volatile materials between 125 and 350°C

(iii) Residual carbon oxidation and burning of volatile materials between 350 and 525°C

4.3.2. Gasification. Gasification is an oxidation process that converts biomass into a gas through the action of a gasifier [59]. When the treatment is carried out by high temperatures above 1200°C, the result is known as synthesis gas composed of H2 and CO; on the other hand, at low processing temperatures, the product includes CH4 and CO2 with impurities of other compounds [56]. The resulting biogas has a calorific value of 4.5–6 MJ/m3; however, this value depends on the type of biomass from which it comes. The calorific
value of biogas represents 10–50% of the calorific value compared to natural gas [57].

The resulting biogas can be used directly; nevertheless, this product can be transformed, through the application of different processes, into other types of fuels and chemical products [61]. The thermochemical process is more efficient compared to combustion and pyrolysis; in addition, it has been reported that gasification is the best process to generate hydrogen gas from biomass [58].

4.3.3. Pyrolysis. Pyrolysis consists of the application of specific temperatures for the transformation of biomass into solid, liquid, and gaseous products [57]. The types of resulting products are H₂, CH₄, CO, and CO₂ as gaseous compounds, for liquids with tar and oils, as well as solid compounds [58, 61]. This process is carried out in a temperature range of 400–800°C without the presence of oxygen. The quality and performance of the resulting biofuel depend on factors such as time, temperature, biomass composition, and process specifications; forestry and agricultural residues are suitable biomass for the production of biofuels, as a product oil with a calorific value of 38 MJ/kg is obtained [59].

The main application of the pyrolysis process is to obtain charcoal; however, the production of liquid biofuels has increased in the last decade at temperatures of approximately 500°C [56]. The classification of the pyrolysis process is based on the applied temperature range; carbonization occurs between 300 and 500°C, slow pyrolysis around 500°C, fast pyrolysis between 500 and 650°C, and finally, flash pyrolysis at temperatures above 650°C [57].

4.3.4. Liquefaction. Liquefaction is also called hydrothermal liquefaction [56], and it is carried out in an aqueous medium with the application of temperature between 280 and 370°C and high pressure of 10–25 MPa [57]. This type of technology can be used for different types of biomass; nevertheless, algae residues are ideal because this technology omits the drying of the biomass, compared to the pyrolysis process, which means significant savings in energy consumption [61].

The main product obtained from the liquefaction process is bio-oil, which has a calorific value of 30–35 MJ/kg, which can be transformed into different biofuels [62]. In this sense, the liquefaction process involves repolymerization reactions for the transformation of bio-oil, chemical products, solid waste, and gas [58].

5. Biofuels from Cocoa Industrial Wastes

Biofuel is defined as a solid, liquid, or gaseous fuel mainly generated from biomass [63]. These can be classified into first-, second-, and third-generation biofuels. Those of the first generation are obtained from food sources such as sugar, vegetable oils, and starches, while those of the second are those of lignocellulosic biomass and those of the third are those that are produced from aquatic materials such as algae [63]. An advantage of biofuels is that they produce less emissions of SO₂, NOₓ, and soot than conventional fossil fuels since they have a minimum content of sulfur, nitrogen, and ash, which represents an advantage when using them [64]. In Figure 3, the general cycle for obtaining biofuels from cocoa industrial wastes is shown.

5.1. Biochar. Biochar is produced with the transformation of biomass by thermochemical treatments [65]. This change produces a solid residue, along with a bio-oil and a gas composed of hydrogen, carbon oxides, and hydrocarbons [66]. The use of CPH in the generation of biochar uses temperatures between 400 and 800°C; however, alternatives to the process with high temperatures are sought because the biochar produced at 500°C presents high pH and decreased performance in general [67].

5.2. Bioethanol. Bioethanol is obtained from the fermentation of sugars by the action of yeasts. In general, starch-rich raw materials are used. The use of lignocellulosic material is possible through a pretreatment that hydrolyzes cellulose into glucose to generate fermentation [68]. The demand for bioethanol has increased the development of technically and economically feasible procedures; these are based on the use of biomass or a fraction of it [69]. Obtaining bioethanol is possible using different raw materials; therefore, first-, second-, and third-generation bioethanol is obtained [70]. Cocoa residues are a good source for the production of bioethanol because the different by-products contain various chemical compounds.

5.3. Biogas. Biogas is a renewable fuel that is produced from the anaerobic digestion of organic material (such as waste and residues from agriculture and the food industry) [71]. During this metabolic pathway, organic carbon is converted through oxidation-reduction reactions into 30–50% carbon dioxide (CO₂, its most oxidized state) and 50–70% methane (CH₄, its lowest form) [72]. Biogas can also contain 0–3% nitrogen, 5–10% water vapor, 0–1% oxygen, and some others corresponding to less than 1%, such as hydrogen sulfide, ammonia, hydrocarbons, and siloxanes. [73]. This fuel can be used to produce electricity, heat, or as a fuel for vehicles, with environmental, climatic, and economic benefits [71].

5.4. Biohydrogen. Biohydrogen is a sustainable fuel produced in its economical form by microbes through fermentation [74]. However, this product can be obtained from different biomass and with various thermochemical processes [75]. There are some complications to producing biohydrogen on a large scale and commercially; the alternatives to increase production efficiency are based on the application of pretreatments to augment the bioavailability of simple sugars in biomass [76]. Biohydrogen is considered the most ecological fuel; the waste from its processing is water vapor; its calorific value (142 MJ/kg) is higher than the value of methane, natural gas, and even gasoline [77].
5.5. Bio-Oil. Bio-oil is a mixture of organic compounds obtained from the pyrolysis of biomass. Among these compounds are sugar monomers and oligomers, as well as sugar derivatives, such as carboxylic acids, aldehydes, ketones, esters, and alcohols [78]. The abundant presence of carboxylic acids makes the bio-oil corrosive. The water content ranges between 20 and 30% depending on the nature of the biomass, which reduces its calorific value and viscosity; the main applications of bio-oil are low-quality boiler fuel, high-quality car engine fuel after upgrade, sources of value-added chemicals, functional carbon materials, and binders [79]. Some researchers develop methods to upgrade bio-oil into biofuel through hydrodeoxygenation, as well as studying strategies based on biomass pretreatments such as dry torrefaction, wet torrefaction, acid and alkaline treatment, steam explosion, downstream treatment of bio-oil such as emulsification, solvent addition, or filtration [80].

5.6. Liquid Smoke. Liquid smoke is a liquid product that is generated from the decomposition process of organic waste or from the condensation of smoke generated in the burning of biomass [81]. This liquid can be extracted from biomass by rapid pyrolysis. This process is carried out at a medium temperature and with high biomass flows [82]. Rapid pyrolysis of biomass is a thermochemical conversion process to produce biofuels. During this process, heavy tar, light tar (liquid smoke), charcoal, and uncondensed gases are produced [83]. Liquid smoke is also known as wood vinegar, pyrolysis liquid, pyrolysis oil, bio-crude oil, biofuel oil, pyrolygous tar, pyrolygous acid, wood liquid, and wood oil [82]. Table 3 shows studies of the production of biofuels from cocoa by-products.

6. Future Trends of Biofuels from Cocoa By-Products

The trends for the generation of fuels from cocoa lignocellulosic biomass explore the alternatives to use catalysts that accelerate and increase the reactions in the conversion of compounds used in the process. This is because recent studies determine that the use of catalysts produced from agricultural residues is an economically and ecologically feasible alternative [96]. The most promising proposals are based on the use of alkaline, acid, and enzyme catalysts that simplify operations by easily recovering from the mixture [97]. Other aspects to consider in the future are the optimization of the pretreatments for the variables of the process; some investigations use the statistical method of response surface to determine the precise conditions in obtaining biofuels [98].

Some aspects to be resolved in the future are the modernization of the technology used for the conversion and treatments of biomass; these include aspects such as temperature control, industrial capacity, and specialized equipment [63, 99]. In addition, obtaining an adequate and continuous supply of material as a source for the production of biofuels is a particular issue; each time they gain greater relevance due to the development of economies based on this activity, which, in turn, generate new policies, minimize the effects negative to the environment, and avoid biological risks in agroecosystems [100].

The main problem in the production of lignocellulosic biomass biofuels is the staggering at the industrial and commercial level; this is due to the type of technology to be used for the different residues generated from the agroindustry. However, this problem has been addressed by different investigations in recent years with the implementation of strategies to optimize the generation of fuels from lignocellulosic biomass [101].
| Product   | Biomass | Process                                                                 | Results                                                                                                     | Reference |
|-----------|---------|------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|-----------|
| Biochar   | CPH     | Low-temperature pyrolysis with residence times of 30–120 minutes in 30-minute intervals. | Biochar with a caloric value of 17.8 MJ/kg with high potassium content. The resulting biofuel has characteristics similar to lignite. | [40]      |
| Biochar   | CPH     | Pyrolysis at temperatures of 250, 300, and 350°C. Activation process with HCl to reduce the values of free fatty acids to use cooking oil used in the production of biodiesel. | The activated carbon generated from CPH showed better retention of free fatty acids than the esterification treatment with H2SO4. | [84]      |
| Bioethanol| CPH     | Fermentation using *Zymomonas mobilis* in a period of 0–8 days. The percentages of microorganisms added were 8–16% v/v. | An alcohol graduation of 10.62% was obtained under 8 day conditions with a concentration of 14% v/v. | [85]      |
| Bioethanol| CM      | Fermentation using *Pichia kudriavzevii* for 5 days at a temperature of 30°C. | The result shows that the maximum ethanol concentration was 13.8 g/L. | [86]      |
| Bioethanol| CBS     | Fermentation with variation in the amount of yeasts during 6 days of the process; hydrolisis pretreatment with H2SO4 at temperatures of 30–80°C in periods of 50–150 minutes. | 8.46% bioethanol was produced under pH 8 conditions, with a yeast concentration for fermentation of 0.05 mg/g in 6 days of the process. pH was determined to be the main influencing factor. | [87]      |
| Biogas    | CPH     | Fermentation process with the application of four pretreatments, acid (H2SO4), alkaline (H2O2), ground without treatment, and the last one not ground without treatment. | The biogas yields by pretreatment were acid 162.8, alkaline 564.8, ground without treatment 220.8, and unground without treatment 243.3; the highest production was obtained on day 18 of the process. | [88]      |
| Biogas    | CPH     | The aerobic digestion process together with a hydrothermal pretreatment was used at different temperatures (150–220°C) in times of 5–15 minutes. | The untreated CPH biogas production was estimated at 3571 (N)/kgVS, while the biogas production from pretreated biomass was 526.38L(N)/kgVS at 150°C for 15 minutes. The biogas produced was obtained in a concentration of 66.07% with a yield of 0.734 m3CH4/kgVS. | [89]      |
| Biogas    | CM      | Fermentation process for 25 days with a pretreatment of a NaOH and NaOH-H2O2 solution. | The amount of gas produced daily was measured. The reaction was faster at 55°C, the generation of the product was from the fifth day. The load was determined in 12 gVS/L and the hydrogen production of 703 mL. | [90]      |
| Biohydrogen| CM     | Fermentation process at two temperatures 35°C and 55°C; the organic load of volatile compounds 4, 8, and 12 gVS/L was determined. | The amount of biohydrogen produced was 3674.021 mL, which is equivalent to 91.85 mL H2/gVS. | [45]      |
| Biohydrogen| CM     | Fermentation of the biomass in a load of 10 gVS/L at a temperature of 35 °C at a pH of 5.5 in a period of time of 12 days. | The effect of the pretreatment was compared against an untreated control sample, in which the biomethane production increased from 199 to 226 mL of CH4/gVS. This effect was more relevant for rice straw with an 82% increase. | [91]      |
| Biomethane| CM     | Fermentation for the production of biomethane from lignocellulosic material with a pretreatment with N-methylmorpholine-N-oxide at a temperature of 120°C for 3 hours. | The amount of biomethane produced was 3674.021 mL, which is equivalent to 91.85 mL H2/gVS. | [92]      |
| Bio-oil   | CPH     | Pyrolysis at different temperatures from 300°C–600°C in 100°C steps. | Bio-oil with a calorific value of 36.23 MJ/kg with characteristics similar to diesel. Biogas with a calorific value of 35.24 MJ/kg presented high values of CO2, CO, CH4, H2S, and H2O. The concentration of liquid smoke obtained was 18–23%. The higher speed of heating produced a greater quantity of coal, ash, and water; the calorific power of the product was 22.97 MJ/kg. | [93]      |
| Biogas    | CBS     | Pyrolysis with temperatures of 450, 500, and 550°C with an increase of 5–15°C/minute. | Bio-oil with a calorific value of 36.23 MJ/kg with characteristics similar to diesel. Biogas with a calorific value of 35.24 MJ/kg presented high values of CO2, CO, CH4, H2S, and H2O. The concentration of liquid smoke obtained was 18–23%. The higher speed of heating produced a greater quantity of coal, ash, and water; the calorific power of the product was 22.97 MJ/kg. | [94]      |

**Table 3:** Biofuels generated from cocoa industrial wastes.

CPH = cocoa pod husk; MJ/kg = megajoule/kilogram; H2SO4 = sulfuric acid; HCl = hydrochloric acid; v/v = volume/volume; H2O2 = hydrogen peroxide; VS = volatile solids; CO2 = carbon dioxide; CO = carbon monoxide; CH4 = methane; H2S = hydrogen sulfide; H2O = water; CM = cocoa mucilage; NaOH = sodium hydroxide; L = liter; g = gram; mL = milliliter; pH = potential of hydrogen; mg = milligram; CBS = cocoa bean shell.
7. Conclusions

Food production entails a generation of important wastes for the industry, due to the nutritional quality that they possess even after being considered as nonvalue materials. The challenge is to minimize the negative effect it has on the environment; there are different perspectives to achieve this objective; recovering these wastes and transforming them into new products is an alternative that benefits the integral use of the fruit; this can generate a stable economy around the use of wastes.

The generation of biofuels from by-products of the industry responds to the need to reduce the consumption of fossil fuels and provide a source of sustainable fuels that has the least ecological impact. In this context, cocoa industrial wastes have the potential to be a source of biomass in the production of biofuels, due to their chemical composition, and the amount of waste generated per year worldwide.

Regarding the production of biofuels, CPH was the most versatile by-product for the generation of different biofuels; however, for its better use, it is necessary to apply a pretreatment that allows obtaining rich substrates in compounds for fermentation and subsequent production of liquid and gaseous biofuels. In addition, it contains a significant amount of compounds for the formation of solid biofuels. CBS is the waste that although it contains a higher content of valuable compounds, it contains fewer applications for obtaining biofuels; nevertheless, it is more relevant in other industries such as food, pharmaceuticals, and cosmetics.

Conflicts of Interest

The authors have no conflicts of interest to declare.

Authors’ Contributions

All authors actively participate in the complete preparation of the manuscript.

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