

# *Valorisation strategies for cocoa pod husk and its fractions*

Article

Accepted Version

Creative Commons: Attribution-Noncommercial-No Derivative Works 4.0

Lu, F., Rodriguez Garcia, J. ORCID: <https://orcid.org/0000-0002-4986-3144>, Van Damme, I., Westwood, N. J., Shaw, L., Robinson, J. S. ORCID: <https://orcid.org/0000-0003-1045-4412>, Warren, G., Chatzifragkou, A. ORCID: <https://orcid.org/0000-0002-9255-7871>, McQueen Mason, S., Gomez, L., Faas, L., Balcombe, K., Srinivasan, C. ORCID: <https://orcid.org/0000-0003-2537-7675>, Picchioni, F., Hadley, P. and Charalampopoulos, D. ORCID: <https://orcid.org/0000-0003-1269-8402> (2018) Valorisation strategies for cocoa pod husk and its fractions. *Current Opinion in Green and Sustainable Chemistry*, 14. pp. 80-88. ISSN 2452-2236 doi: 10.1016/j.cogsc.2018.07.007 Available at <https://centaur.reading.ac.uk/79360/>

It is advisable to refer to the publisher's version if you intend to cite from the work. See [Guidance on citing](#).

To link to this article DOI: <http://dx.doi.org/10.1016/j.cogsc.2018.07.007>

Publisher: Elsevier

including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the [End User Agreement](#).

[www.reading.ac.uk/centaur](http://www.reading.ac.uk/centaur)

**CentAUR**

Central Archive at the University of Reading

Reading's research outputs online

# Valorisation strategies for cocoa pod husk and its fractions

Fei Lu<sup>1</sup>, Julia Rodriguez-Garcia<sup>1</sup>, Isabella Van Damme<sup>2</sup>, Nicholas Westwood<sup>3</sup>, Liz Shaw<sup>4</sup>,  
James S. Robinson<sup>4</sup>, Geoff Warren<sup>4</sup>, Afroditi Chatzifragkou<sup>1</sup>, Simon McQueen Mason<sup>5</sup>,  
Leonardo Gomez<sup>5</sup>, Laura Faas<sup>5</sup>, Kelvin Balcombe<sup>6</sup>, Chittur Srinivasan<sup>6</sup>, Fiorella Picchioni<sup>6</sup>,  
Paul Hadley<sup>6</sup>, Dimitris Charalampopoulos<sup>1</sup>

<sup>1</sup> Department of Food and Nutritional Sciences, University of Reading, UK

<sup>2</sup> Mars Wrigley Confectionery UK Ltd, Slough, Berkshire, UK

<sup>3</sup> School of Chemistry and Biomedical Sciences Research Complex, University of St Andrews, UK

<sup>4</sup> Department of Geography and Environmental Sciences, University of Reading, UK,

<sup>5</sup> Department of Biology, University of York, UK

<sup>6</sup> School of Agriculture Policy and Development, University of Reading, UK

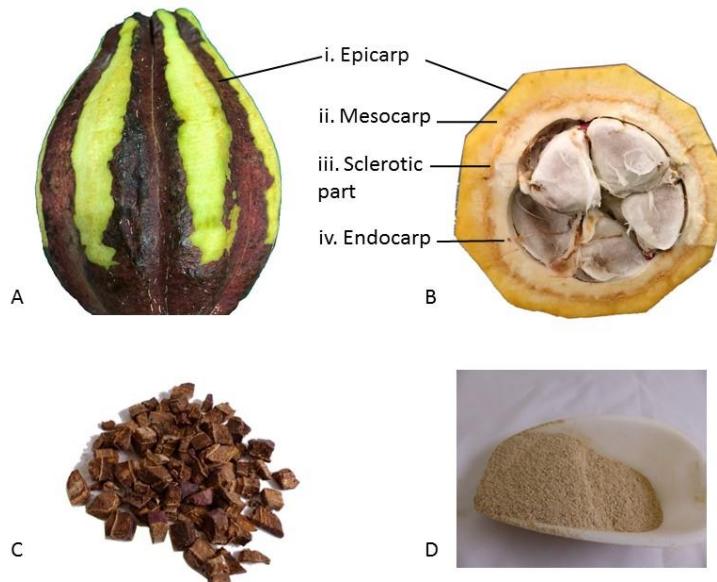
## Abstract

Cocoa pod husk (CPH) is the main by-product (ca. 70-75% weight of whole fruit) of the cocoa harvest, an important and economic crop in developing countries. It is a rich source of minerals (particularly potassium), fibre (including lignin, cellulose, hemicellulose and pectin) and antioxidants (e.g. phenolic acids). An existing practise is the return of CPH to soil with potential benefits (or disadvantages) for cocoa productivity and soil sustainability that have not been fully characterised. Currently, alternative low-value applications of CPH include its use as animal feed, as a starting material for soap making and activated carbon. Other biotechnological valorisation potentials for CPH and its fractions include the production of bio-fuels and their incorporation in food systems. Physical, chemical or biological pre-treatment approaches are needed in order to achieve desirable fractions in a cost-effective and sustainable manner for novel applications in food and non-food sectors.

**Keywords:** Cocoa pod husk, valorisation, extraction, pre-treatment

## 1. Introduction

Cocoa (*Theobroma cacao L*) is an important and economic crop in developing countries. The production of cocoa beans in 2016-2017 was 4.7 million tonnes worldwide [1]. Cote D'Ivoire, Ghana and Indonesia are the top three producers of cocoa beans, contributing to 67% of the global production. Large quantities of underexploited by-products, including cocoa pod husk (CPH) and pulp, are generated by removing the beans from the cocoa pods [2]. CPH weighs about 75% of the whole fruit and is the main process by-product [3-5].



**Figure 1: Fresh cocoa pod fruit (A and B) and dried CPH (C and D) from Indonesia. A: Fresh cocoa pod fruit in which epicarp (in dark brown) has been partially peeled. B: Transverse section of fresh cocoa pod fruit, with the illustration of the separate parts, including epicarp, mesocarp, sclerotic part and endocarp. C: Freeze-dried CPH. D: Milled freeze-dried CPH.**

After removal of the cocoa beans, CPH is usually discarded on the farm and can function as an organic fertiliser, a practice that adds organic matter to soil and enables the return of nutrients to the soil and their recycling to plant-available forms after decomposition

(discussed further in Section 3.1) [6\*, 7]. However, untreated CPH left on the soil surface may act as a source of inoculum for plant diseases such as black pod rot due to the presence of *Phytophthora spp.* [8, 9]. Black pod rot causes an annual yield loss from 20% to 30% worldwide, while individual farms may suffer an annual yield loss from 30% to 90% [10]. CPH is under-exploited as a renewable resource that is rich in dietary fibre, lignin and bioactive antioxidants such as polyphenols [8]. Recovering these lignocellulosic fractions and bioactive compounds may lead into the development of a profitable commodity and subsequently this could bring revenue to farmers, thus promoting economic development [11, 12]. Bioconversion of CPH to added-value products, such as biomaterials for food and non-food uses, it is also a potential approach to maintain the sustainability of cocoa production. The opportunity of valorising CPH towards added-value applications is enormous, given its high abundance and the fact that cocoa is mainly cultivated in developing countries. This review will evaluate existing low-value applications of CPH and the value-added potential of CPH and its fractions in food applications based on CPH's chemical composition.

## 2. Chemical composition of cocoa pod husk

CPH comprises the epicarp, mesocarp, sclerotic part and endocarp (Figure 1). Table 1 shows the chemical composition of an example of a CPH from Ghana. The CPH consists primarily of fibrous materials including 19.7-26.1% cellulose, 8.7-12.8% hemicellulose, 14-28% lignin and 6.0-12.6 % pectin. The epicarp is enriched with lignin, while the mesocarp contains mainly (~50%) cellulose and the endocarp is rich in pectic substances [13]. Xylan, arabinoxylan and arabinan are the main hemicellulose in CPH that have been deduced from the high amount of isolable arabinose and xylose [14]. Other hemicelluloses such as xyloglucans, galactomannans or (galacto) glucomannans can also be found in CPH [9]. Lignin is a complex aromatic heteropolymer, made from phenylpropane units (*p*-coumaryl, coniferyl and sinapyl alcohols) and is strongly attached to cellulose and hemicellulose, providing rigidity to the plant cell wall [15, 16]. Condensed tannins have highly polymerized structures and could be bound to lignin in CPH with a dry weight content of 5.2% [8]. Pectin that is associated with cellulose and hemicellulose is determined as uronic acids, contributing to 6.7-12.4% of CPH [8, 9]. The ash content of CPH ranges from 6.4-8.4% w/w with a variety of minerals. Significantly high amounts of K (2.8-3.8% w/w) are observed, followed by Ca, Mg and P [9]. CPH is also a source of phenolic acids, ranging from 4.6 to 6.9g GAE/100g.

**Table 1: Chemical Composition of cocoa pod husk [9, 17-19]**

Composition	Amount (%, w/w, dry weight)
Protein	7-10
Fat	1.5-2
Carbohydrates	32-47
Cellulose	19.7-26.1
Hemicellulose	8.7-12.8
(Xylan & arabinoxylan)	
Lignin	14-28
Pectin	6.0-12.6
Ash	6.4-8.4
Minerals	
K	2.8-3.8
Ca	0.25-0.46
Mg	0.11-0.25
P	0.19
Na	0.01-0.02
Fe	0.003-0.006
Phenolic content (g GAE <sup>1</sup> /100g)	4.6-6.9

<sup>1</sup> Gallic acid equivalent

### 3. Low value applications of CPH

#### 3.1 Fertiliser and soil organic matter

The high mineral content of CPH, particularly in K, Ca and P, offers the possibility for partially substituting conventional fertilisers, based on research from Nigeria and Ghana [5\*\*, 17]. One study in Nigeria reported that combining CPH powder with basal phosphorus fertiliser could achieve similar plant quality, seed yield and harvest index of black benniseed cultivation, compared to NPK fertiliser (mixture of  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{P}_2\text{O}_5$  and  $\text{K}_2\text{O}$ ) [7]. Other studies have focused on the use of CPH ash as a fertiliser; replacing up to 50% conventional NPK fertiliser with CPH ash had a positive effect on grain yield and nutrients uptake in maize production [20] and on fruit growth, yield and soil fertility in tomato production [21]. Such eco-friendly applications could potentially replenish the shortage of expensive NPK fertiliser due to limited distribution and marketing for fertiliser procurement in developing countries such as Ghana. Burning CPH to produce ash might also have additional benefits in terms of improved farm sanitation and control of a potential source of inoculum for black pod rot disease [20]. To demonstrate the economic feasibility of using CPH fertiliser in cocoa farming, a study in Nigeria has compared the gross margin of cocoa production between

farmers using CPH fertiliser and farmers not using CPH fertiliser [22]. The study showed that farmers using CPH fertiliser achieved approximately three times more profit per hectare, compared with farmers that did not use it.

In addition to being a source of mineral nutrients, CPH has organic macromolecules such as cellulose, hemicellulose, lignin and protein as major constituents (Table 1) and thus will also provide an input of organic matter when returned to soil in a fresh (i.e. non-burnt) state. Soil organic matter (SOM) is a key constituent of soils in cropping systems because not only does its decomposition release nutrients to crops, as mentioned above, but also it increases the capacity of soil to retain nutrients and water and to resist erosion when built up [23]. Conversion of native forest systems to cocoa cultivation frequently depletes SOM [24] as a result of physical disturbance and lack of replenishment of organic matter exported from the system with each crop [25]. Such decline in SOM has been linked to declines in cocoa productivity and bean quality with time since land conversion to cocoa farms [26]. To our knowledge, there is currently no information on consequences of CPH return to soil on the stocks and forms of SOM in cocoa systems. However, CPH might be an important source of SOM to lessen the severity of SOM depletion (and associated soil fertility decline) on land conversion and should be considered when evaluating the alternative applications of CPH as discussed in subsequent sections.

### **3.2 Soap making**

CPH could also be a starting material for soap making in western African countries, through a process that includes steps of ashing, leaching, filtration and concentration, saponification, cooling and cutting. After burning CPH in air into an ash containing  $K_2O$ , the ashes were leached with water and correspondingly generated CPH potash (potassium hydroxide, KOH), each tonne of fresh pod husk would generate about 6 kg potash [17]. The potash could be further filtrated, concentrated and used in saponification with oil to produce soaps [27]. CPH derived soaps have been successfully produced in pilot plant scale with detailed market research in Ghana and other African countries [17]. Soaps made with CPH potash have great solubility, consistency, cleansing and lathering ability, compared to soaps made with chemical KOH [28]. Results also showed that the commercialization of soap with CPH potash is highly feasible, and mainly driven by the demand for natural and less harsh toiletry products [17]. As CPH is abundant and readily available in these countries, using natural raw materials could also ease the financial pressure of importing chemicals for developing

countries. A market report in Ghana showed that 3 tonnes of liquid soap made by CPH potash could bring the profit of 63,000 Ghanaian cedi [17]. The successful usage of CPH as a starting material for commercial soap making would also be an alternative way to generating additional income for farmers.

### **3.3 Animal feed**

Another application of CPH is its use as animal feed, particularly for pig, poultry, rabbit and fish, aiming to replace conventional feed ingredients such as maize and bran. This approach has been researched widely in West Africa, Brazil as well as in Malaysia. It has been shown that replacing up to 20% of maize, rice bran and wheat bran mixture with CPH in fish meal (tilapia) did not lead to significant changes in the growth performance, feed and nutrient retention efficiencies of tilapia in Cameroon. This could directly reduce the feeding cost from US\$ 0.37/kg to US\$ 0.35/kg with 20% substitution; correspondingly, for producing each kilogram of fish, the overall cost could decrease from US\$ 0.77 to US\$ 0.68 [29]. However, the effect of CPH inclusion as a feeding ingredient for animals with different digestive systems should be further considered. One study reported that replacing rice bran with up to 30% CPH caused no adverse effect on weight gain and final body weight of rabbits [30]. Others reported that feeds with more than 10% CPH could have an adverse effect on the growth of poultry [31]. The latter could be due to the high fibre content of CPH, which most likely reduced their digestibility and increased gut viscosity in these monogastric animals [32]. This may have undesirable effect on body mass gained by animals. However, recent studies have shown that the pre-treatment of CPH with multiple enzymes, i.e. Viscozyme and Pectinex [19] and fungus (*Phanerochaete chrysosporium*) [33], could increase CPH digestibility by about 30%, thus making it suitable for poultry as well as steers. The above studies highlight the potential of utilising CPH in the agricultural sector as animal feed, in order to substitute costly conventional feeding ingredients and diminish any potential environmental effect by reducing CPH disposal on the farm.

### **3.4 Activated carbon**

Activated carbon may also be produced from CPH, through physical or chemical activation. Carbonisation and activation involve physical/thermal processing. In a recent study, CPH was heat dried at 500°C with a N<sub>2</sub> flow (carbonisation), followed by applying a CO<sub>2</sub> flow at 650-850°C for 30 min (activation) [34]. This process yielded 18-38% (w/w) of activated carbon with a surface area of 1.1 m<sup>2</sup>/g. However, pre-treatment of CPH with hydrochloric acid (HCl)

significantly reduced the ash content of the CPH, resulting in the production of activated carbon with higher surface area ( $356\text{ m}^2/\text{g}$ ) using lower temperatures ( $650^\circ\text{C}$  vs  $900^\circ\text{C}$ ) [34]. Chemical activation of CPH involves the usage of agents such as  $\text{K}_2\text{CO}_3$ ,  $\text{KOH}$  and  $\text{ZnCl}_2$  under nitrogen at temperatures of  $500^\circ\text{C}$  -  $800^\circ\text{C}$ , yielding 13.5-47.2% of activated carbon with a much larger surface area ( $780\text{ m}^2/\text{g}$ ) [35]. The above-mentioned studies indicate that CPH could be utilised as an alternative source for activated carbon production, delivering a high surface area and high adsorption capacity given proper treatment. The low price of CPH, compared to traditional precursors such as anthracite, coal or peat, could enhance its economic potential with a reduction in overall production costs [36].

#### **4. Current and potential high value applications of CPH and fractions**

To date, owing to its high lignocellulosic content, CPH has been explored as a starting material for paper making [3] and to a lesser extend as a substrate for the production of bio-fuels and platform chemicals [11, 18, 37].

##### **4.1 Paper making**

Studies on the replacement of wood fibre with plant-based fibre including CPH for paper making applications have been carried out in Malaysia [3]. From a processing point of view, an initial step is the dissolution of the biomass in an alkali solution, i.e. 20%  $\text{NaOH}$  at high temperature to obtain a pulp. The quality of the pulp is directly affected by the chemical composition of the lignocellulosic materials, where a material with high cellulose (34%), low lignin (<30%) and low ash content is preferred [38]. Comparable amounts of cellulosic and hemicellulosic content in both CPH and the wood fibres usually used in paper making have been reported. However, delignification is necessary during the pulping process for lignocellulosic materials such as CPH, in order to avoid the negative effects of lignin on paper performance and paper quality. Chemicals, such as sodium sulphide, are involved for dissolving the lignin bound to the fibre [38]. Another important parameter is the physical surface morphology of the biomass. Fibre properties including length, diameter, lumen width and thickness play important roles in tearing resistance, bearing and strength of the paper that is required for various uses. Pulp with shorter and thinner fibre is favoured for porous speciality tissues, for example, tea bag papers, while pulp with longer fibre is usually stronger and thicker and is preferred for high-tear and tensile strength speciality paper, such as bank notes [39]. There are few studies investigating the fibre properties of CPH, and only one showed CPH to possess a linear fibrillar morphology, which might promise the strength

properties required for pulp and paper production [3]. Thus, further evaluation of the fibre properties of CPH should be carried out to validate the selective use of CPH on paper making.

## 4.2 Biofuels and chemical industry

The exploitation of abundant, renewable and inexpensive lignocellulosic biomass resources (e.g. corn, wheat and rice stalk/hull, etc.) as substrates of microbial fermentation for the production of biofuels has been extensively investigated in the last 10 years, with the aim of identifying sustainable energy resources for the future without additional net release of greenhouse gas [37\*, 40]. The fundamental process of biofuel production from lignocellulosic biomass through fermentation involves pre-treatment steps in order to increase the susceptibility of cellulose /hemicellulose to enzymatic hydrolysis, leading to the production of assimilable monosaccharides. The enzymatic hydrolysis of lignocellulosic biomass results in a liquor containing mixtures of hexose and pentose sugars, fermented by yeast strains, such as *Saccharomyces cerevisiae*, *Kluyveromyces marxianus* and *Pichia stipites* [41, 42]. The potential of CPH as a fermentation feedstock has not yet been investigated in practice. However, a recent study estimated theoretically the production of bioethanol from CPH, based on its lignocellulosic composition and several bioconversion factors (i.e. hydrolysis factor and ethanol conversion factor) [42]. They reported that the yield of bioethanol from CPH in theory could be around 0.28 L ethanol (kg TS)<sup>-1</sup>, which is lower than those from maize cobs (~0.51 L ethanol (kg TS)<sup>-1</sup>) and rice straw (~0.49 L ethanol (kg TS)<sup>-1</sup>), as the latter contain higher amount of carbohydrates. Unlike maize cobs and rice straws with low lignin content, handling CPH with high-lignin amounts requires additional processing steps such as, delignification and/or pre-treatment, to separate lignin from cellulose and hemicellulose. It can be achieved through a number of technologies including (1) chemical, i.e. acid or alkali extraction or the use of organic solvents, (2) physical, i.e. steam explosion, and (3) biological, i.e. enzymatic hydrolysis.

Pre-treatment of CPH has been carried out using chemicals, e.g., acidic or alkaline or organic solvents, to enhance the release of cellulose and obtain more fermentable sugars [43]. Previous studies revealed that the lignin content of CPH reduced from 34% to 15% with the following alkali pre-treatment condition: 4% (w/v) NaOH, reaction time of 100 minutes with ratio of biomass/solvent of 1:25 (w/v) [43]. Mild organosolv protocol involves a relative short exposure to high concentration of butanol (95%), with acid (HCl) acting as a catalyst. This

delivers fermentable cellulose and hemicellulose-derived product streams as well as a unique lignin that retains many of its key structural features that is believed to have in the plant [44].

Whilst a long way from industrially relevant, this “lignin-first” view of biomass provides an alternative way of planning valorisation protocols.

Steam explosion is a physical approach that can increase the pore size of lignocellulose materials and ultimately lead to hemicellulose solubilisation and hydrolysis [11]. Steam is applied to the material at high pressure with or without acid/base, resulting in breakage of hydrogen bonds and aryl-ether bonds between cellulose, hemicellulose and lignin [45, 46]. There are studies investigating the effect of lignocellulosic biomass pre-treatment, such as wheat and rice straw by steam-explosion, but there is limited information on CPH. One study reported that combining steam explosion with dilute sulfuric acid impregnation on wheat straw with high-lignin content significantly improved the cellulose conversion into fermentable sugars [47]. This might support the possibility that a combination of chemical/physical/biological pre-treatment of CPH could lead to selective and efficient fractionation of CPH. Factors including temperature, concentration of acid/base and time should be optimized to achieve desirable fractions to maximise the fermentation yield, meanwhile the formation of inhibitors, such as furfural, 5-HMF, ferulic acid and coumaric acid should be minimized [41].

Biological pre-treatment of CPH has been realised through the use of fungal species, as in the case of *Phanerochaete chrysosporium* [33] and *Pleurotus ostreatus* [48]. *Pleurotus ostreatus* showed higher hydrolysis efficiency by reducing cellulose content from 26% w/w to 20% w/w, hemicellulose from 12% to 9% and lignin from 20% to 14% (with the aid of a MnCl<sub>2</sub> catalyst). These results reflect the promising cellulolytic and hemicellulolytic activity of *Pleurotus* species on CPH, which can produce enzymes that will hydrolyse a series of  $\beta$ -(1, 4) linked glucan substrates as well as various glycosides [48]. Enzymatic delignification of biomass utilises oxidases (laccases) and peroxidases (MnPs and LiPs) isolated from white rot fungi, to oxidise both the aromatic rings and aliphatic side chains and generate low-molecular weight compounds [48]. However there have not been many studies on CPH using these systems. The combination of a physical treatment, such as steam explosion/high pressure with enzymatic treatment is suggested, in order to increase the process efficiency and also save refining energy [49].

In many lignocellulosic biomass pre-treatments, lignin is viewed as a necessary evil and the focus is often on its removal at any cost. Increasingly, however, the argument is being made that for a subsidy-free biorefinery to be economically viable, it is necessary to gain more value from the lignin component that arises from, for example, burning it [50, 51]. This has led to extensive studies using other biomass sources into obtaining lignin in a “near to native” form. If achievable, this should facilitate the controlled depolymerisation of lignin to deliver pure aromatic monomers of potential use to the chemical industry.

## 5. Food applications of CPH and fractions

There is an increasing demand by the food industry for novel ‘clean label’ ingredients from natural sources, driven by consumers and regulations [52]. The exploitation of functional components derived from CPH in food applications offers opportunities for developing a novel valorisation chain, as CPH is a source of dietary fibre and antioxidants.

### 5.1 Dietary fibre in CPH

As showed in Table 1, CPH is considered an excellent source of dietary fibre. The total dietary fibre is the sum of soluble dietary fibre (SDF), including pectin,  $\beta$ -glucan and oligosaccharides and some hemicellulose, and insoluble dietary fibre (IDF), such as lignin, cellulose and hemicellulose [11, 53]. It is estimated that pectin is the predominant SDF in CPH based on its mass balance and chemical composition [8]. Pectin is an important ingredient in food products because of its gelling, film-forming and thickening properties, which could provide texture enhancement and stability in food products [9, 54]. Parameters such as pH, time and temperature are key factors generally influencing the extraction process, and consequently the composition and physio-chemical properties of pectin [9, 12, 55, 56]. Solvents previously used for pectin extraction from CPH include water [9], hydrochloric acid [57], nitric acid [58] and citrus acid [59]. High temperature and low pH favours high extraction yields of pectin [12]. Viscosity and viscoelasticity are the two common parameters used to demonstrate the rheological behaviour of pectin in a model system in the literature. A CPH-derived pectin solution extracted using hot water [9] and citric acid [60] exhibited more pseudoplastic properties, compared with commercial apple pomace pectin solutions of the same concentration. However, the CPH-derived pectin had weak gelling behaviour, while the apple pomace pectin performed as a dilute solution. The viscoelastic behaviour of pectin is affected by structural parameters, e.g. the nature of the functional groups on the branched chains and the degree of esterification (DE). The liquid behaviour of apple pectin might be

correlated with a higher DE (58-69%) than DE of CPH pectin extracted by water (42.6%) and citric acid (40.3%) [60]. Scaling-up of pectin extraction from CPH can also be economically feasible, provided that two fundamental steps are considered; the preparation of the raw material (drying and decreasing particle size) and acid used in the hydrolysis (citric acid). If the direct and indirect costs of facilities are also considered, this would give an internal rate of return of 33% and a 4 years investment recovery, which indicates its profitability [61].

Developing SDF enriched food could be beneficial for consumers with dietary fibre intake deficiency and weight management, as nutritionally SDF can retain water, increase satisfaction after eating and decrease the absorption of glucose in the small intestine [62]. Only a few studies have incorporated CPH into real food system including bread [63] and muffins [64\*] and evaluated its contribution towards the textural and organoleptic properties. Applying enzymatic pre-treatment on CPH powder could enrich the amount of SD and potentially act as a fat replacer. Partially (25-75%) replacing vegetable oil with pre-treated CPH powder in a chocolate muffin could, for example, achieve higher moisture, a more tender and a crumbly texture, compared with control samples. However, loss of height, a bitter taste and surface stickiness are the limitations that require improvement in this case [64\*].

Besides SDF, IDF also shows the ability to adsorb and retain water within its fibrous matrix, but it does not form a viscous solution [15]. 52-74% IDF is present in CPH, consisting of cellulose, hemicellulose and lignin (Table 1). A very limited number of studies have investigated the IDF from CPH as functional ingredient into food products. In one study, whole meal flour has been replaced with CPH powder (with no pre-treatment) in a bread formulation, to develop high fibre bread [63]. The results showed that bread with CPH became denser and harder in texture indicating that the texture and quality of the food products are affected significantly by the functionality of fibre and its behaviour during food processing.

SDF is resistant to digestion in the small intestine, but easily fermented in the large intestine; while IDF has very limited digestibility in the human gastrointestinal tract, hence leading to laxation benefits. Thus, a natural source containing dietary fibre with a balanced ratio between SDF and IDF is favoured by the food industry [65]. Since CPH contains much higher IDF than SDF, a chemical pre-treatment of CPH, e.g. hydrolysing with acids/water, could solubilise uronic acids within the IDF and increase the amount of SDF [66]. Although

incorporating CPH into food products is still challenging because of the lower consumer perception and less desirable texture, adjusting the ratios between SDF and IDF of CPH via appropriate pre-treatment could be an alternative approach for adding nutritional value of CPH into food application with promising eating quality. Thus, the addition of pre-treated CPH to food products can: (1) complement dietary fibre content; (2) improve the ratio of IDF to SDF and (3) reduce calorie intake.

## 5.2 Dietary antioxidants - Phenolics

CPH is also a potential source of phenolics/antioxidants, which could be employed as a natural ingredient in value-added products. Total phenolic content (TPC) of fresh CPH is ~ 2-3mg GAE/g. Phenolics, such as flavan-3-ol compounds, including monomers, e.g., catechin and epicatechin, and dimers, i.e. procyanidin have been found in cocoa related products previously [59, 67]. In terms of the composition of phenolic compounds in CPH, catechin, quercetin, (-)-epicatechin, gallic, coumaric, and protocatechuic acids have been identified in dried CPH [68]. The antioxidant capacity of CPH was determined to be 24-42  $\mu$ M Trolox Equivalent (TE)/g in an ABTS assay, 18-34  $\mu$ M TE/g in a DPPH assay and 0.7-2  $\mu$ M TE/g in a FRAP assay, which was higher than other cocoa related by-products such as the cocoa bean shell, cocoa mucilage and other by-products such as tomato peels [67]. A study has demonstrated the ability of CPH extracts as functional ingredients in anti-wrinkle cosmetic products. They applied a gel enriched with CPH extracts on human dermal fibroblast adult cells for 3-5 weeks and found that CPH gel could significantly reduce wrinkles on skin cells and the skin hydration level was improved at the same time [69].

In a conceptual valorisation process of CPH, the fresh husk would need to be dried to ensure material stability and then transferred to a centralised processing facility. Different drying methods including hot air drying, microwave drying and freeze drying could affect phenolic content significantly because of microstructural changes and results showed that freeze-drying and microwave-drying could prevent TPC loss compared to hot air drying [68].

Common extraction methods of phenolic compounds from CPH include the use of organic solvents. The efficiency of extraction may vary according to the chemical properties of organic solvents. TPC of CPH extracted by a mixture of methanol and acetone is reported to be higher than that of ethanol (2 mg GAE/g vs 3.6 mg GAE/g), due to different solubilities [67]. Supercritical fluid extraction (SFE), regarded as a green technology, was also used to extract phenolic compounds from CPH in a recent study [70]. The highest TPC (12.97 mg

GAE/g) was determined in the CPH extract with the optimum conditions of 60 °C, 299 bar and 13.7% of ethanol. This result implies that CPH-derived supercritical extracts with high phenolic content could be potentially used as natural antioxidants in food applications, which could improve the food products' shelf life by acting as a natural preservative.

## **6. Conclusions**

CPH is a good source of lignocellulosic content, pectin, potash and phenolics. As an important economic crop in developing countries, the valorisation of CPH and its fractions by developing end-user applications in the food and non-food sector is regarded as beneficial for several stakeholders, including farmers, industries, consumers and academic researchers. Currently, low-value applications of CPH hold promise in animal feed and the cosmetic/personal hygiene industry. However biotechnological and food applications of CPH and its fractions are still under exploration. Future studies should focus on the optimal pre-treatment processes of CPH, to obtain desirable fractions that are applicable in food systems with improved nutritional value and amenable for bioconversion into energy supply. With the identification of product applications with a high commercial value, there is a need to develop/improve clean and sustainable technologies that are easy to process, cost-effective and environmentally friendly, to convert them into high value-added products. Successful conversion of CPH into biofuels could prevent significant consumption of fuel/diesel and the production of greenhouse gas, in order to enhance environmental sustainability. Improved knowledge on the consequences of the current practice of CPH return to soil (as an organic fertiliser) for cocoa productivity and soil sustainability in low input farming systems is required to inform holistic decisions on valorisation routes for CPH.

## **Acknowledgments**

The authors would like to acknowledge the Biological Sciences Research Council (BBSRC) and Mars Wrigley Confectionery for their financial support on a collaborative Global Challenges Research Fund (GCRF) project entitled “Development of novel value chain from cocoa pod husks in Indonesia: Technological, environmental and socio-economic challenges of a value chain” (BB/P022995/1).

## Declaration of conflict of interest

Authors would like to declare no conflict of interest.

## References:

1. ICCO. *Quarterly Bulletin of Cocoa Statistics*. 2017 [cited 2018 05/03/2018]; Available from: <https://www.icco.org/about-us/icco-news/380-quarterly-bulletin-of-cocoa-statistics-november-2017.html>.
2. FAOSTAT. *Chocolate: facts and figures*. 2015 [cited 2018 17/03]; Available from: <http://www.fao.org/resources/infographics/infographics-details/en/c/277756/>.
3. Daud, Z., et al., *Chemical Composition and Morphological of Cocoa Pod Husks and Cassava Peels for Pulp and Paper Production*. Australian Journal of Basic and Applied Sciences, 2013. **7**(9): p. 406-411.
4. Adjin-Tetteh, M., et al., *Thermochemical conversion and characterization of cocoa pod husks a potential agricultural waste from Ghana*. Industrial Crops and Products, 2018.
- 5\*\*. Perez, E., et al., *Chocolate: Cocoa byproducts technology, rheology, styling and nutrition. Chapter 10: Proximal composition and the nutritional and functional properties of cocoa by-products (pods and husks) for their use in the food industry.*, ed. E.P. Sira. 2015, New York: Nova Science Publishers, Inc.

**A book chapter focusing on compositional, nutritional and functional properties of cocoa pod husks.**

- 6\*. Syamsiro, M., et al., *A preliminary study on use of cocoa pod husk as a renewable source of energy in Indonesia*. Energy for Sustainable Development, 2012. **16**(1): p. 74-77.

**A comprehensive summary on producing bio-ethanol by using cocoa pod husks.**

7. Aboyeji, et al., *Influence of cocoa pod husk powder on the performance of black benniseed under basal application phosphorus fertilizer in the Southern Guinea Savannah of Nigeria*. Advances in Environmental Biology, 2016. **10**: p. 78+.
8. Yapo, B.M., et al., *Adding Value to Cacao Pod Husks as a Potential Antioxidant-Dietary Fiber Source*. American Journal of Food and Nutrition, 2013. **1**(3): p. 38-46.
9. Vriesmann, L.C., R.D. de Mello Castanho Amboni, and C.L. de Oliveira Petkowicz, *Cacao pod husks (*Theobroma cacao* L.): Composition and hot-water-soluble pectins*. Industrial Crops and Products, 2011b. **34**(1): p. 1173-1181.
10. Acebo-Guerrero, Y., et al., *Management of black pod rot in cacao (*Theobroma cacao* L.): a review*. Fruits, 2011. **67**(1): p. 41-48.
11. Igbinadolor, R.O. and A.A. Onilude, *Bioprocess systems applied for the production of bio-ethanol from lignocellulosic biomass of cocoa pod husk (*Theobroma cacao* L.) and other agricultural residues: A review*. African Journal of Biotechnology, 2013. **12**(35): p. 5375-5388.
12. Vriesmann, L.C., R.F. Teófilo, and C.L.d.O. Petkowicz, *Optimization of nitric acid-mediated extraction of pectin from cacao pod husks (*Theobroma cacao* L.) using response surface methodology*. Carbohydrate Polymers, 2011a. **84**(4): p. 1230-1236.
13. Sobamiwa, O. and O.G. Longe, *Utilization of cocoa-pod pericarp fractions in broiler chick diets*. Animal Feed Science and Technology, 1994. **47**(3): p. 237-244.
14. Serra Bonvehí, J. and M. Aragay Benería, *Composition of dietary fibre in cocoa husk*. Zeitschrift für Lebensmitteluntersuchung und -Forschung A, 1998. **207**(2): p. 105-109.
15. Lecumberri, E., et al., *Dietary fibre composition, antioxidant capacity and physico-chemical properties of a fibre-rich product from cocoa (*Theobroma cacao* L.)*. Food Chemistry, 2007. **104**(3): p. 948-954.

16. Das, H. and S.K. Singh, *Useful Byproducts from Cellulosic Wastes of Agriculture and Food Industry—A Critical Appraisal*. Critical Reviews in Food Science and Nutrition, 2004. **44**(2): p. 77-89.
17. Gyedu-Akoto, E., et al., *Natural Skin-care Products: The Case of Soap Made from Cocoa Pod Husk Potash*. Advances in Research, 2015. **4**(6): p. 365-370.
18. Mansur, D., et al., *Conversion of cacao pod husks by pyrolysis and catalytic reaction to produce useful chemicals*. Biomass and Bioenergy, 2014. **66**: p. 275-285.
19. Alemaowor, F., et al., *Enzyme cocktail for enhancing poultry utilisation of cocoa pod husk*. Scientific Research and Essay, 2009. **4**(6): p. 555-559.
20. Ayeni, L.S., et al., *Comparative and Cumulative Effect of Cocoa Pod Husk Ash and Poultry Manure on Soil and Maize Nutrient Contents and Yield*. American-Eurasian Journal of Sustainable Agriculture, 2008. **2**(1): p. 92-97.
21. Ayeni, L.S., *Integrated Application of Cocoa Pod Ash and NPK Fertilizer on Soil Chemical Properties and Yield of Tomato*. American-Eurasian Journal of Sustainable Agriculture, 2008. **2**(3): p. 333-337.
22. Agbeniyi, S.O., K.A. Oluyole, and M.O. Ogunlade, *Impact of Cocoa Pod Husk Fertilizer on Cocoa Production in Nigeria*. World Journal of Agricultural Sciences, 2011. **7**(2): p. 113-116.
23. Lal, R., *Soil Carbon Sequestration Impacts on Global Climate Change and Food Security*. Science, 2004. **304**(5677): p. 1623-1627.
24. van Straaten, O., et al., *Conversion of lowland tropical forests to tree cash crop plantations loses up to one-half of stored soil organic carbon*. Proceedings of the National Academy of Sciences, 2015. **112**(32): p. 9956-9960.
25. Blaser, W.J., et al., *Shade trees have limited benefits for soil fertility in cocoa agroforests*. Agriculture, Ecosystems & Environment, 2017. **243**: p. 83-91.
26. McMahon, P., et al., *Testing local cocoa selections in three provinces in Sulawesi: (i) Productivity and resistance to cocoa pod borer and Phytophthora pod rot (black pod)*. Crop Protection, 2015. **70**: p. 28-39.
27. Onyegbado, C.O., E.T. Iyagba, and O.J. Offor, *Solid soap production using plantain peel ash as source of alkali*. Journal of Applied Sciences & Environmental Management, 2002. **6**(1): p. 73-77.
28. Taiwo, O.E. and F.A.O. Osinowo, *Evaluation of various agro-wastes for traditional black soap production*. Bioresource Technology, 2001. **79**(1): p. 95-97.
29. Pouomogne, V., T. Gabriel, and J.B. Pouemegne, *A preliminary evaluation of cacao husks diets for juvenile Nile tilapia (*Oreochromis niloticus*)*. Aquaculture, 1997. **156**: p. 211-219.
30. Ridzwan, B.H., et al., *Evaluation of cocoa-pod husks on performance of rabbits*. Animal Feed Science and Technology, 1993. **40**(2): p. 267-272.
31. Oddoye, E.O.K., C.K. Agyente-Badu, and E. Gyedu-Akoto, *Cocoa and Its By-Products: Identification and Utilization*, in *Chocolate in Health and Nutrition*, R.R. Watson, V.R. Preedy, and S. Zibadi, Editors. 2013, Humana Press: Totowa, NJ. p. 23-37.
32. Lateef, A., et al., *Improving the quality of agro-wastes by solid-state fermentation: enhanced antioxidant activities and nutritional qualities*. World Journal of Microbiology and Biotechnology, 2008. **24**(10): p. 2369-2374.
33. Laconi, E.B. and A. Jayanegara, *Improving Nutritional Quality of Cocoa Pod (*Theobroma cacao*) through Chemical and Biological Treatments for Ruminant Feeding: In vitro and In vivo Evaluation*. Asian Australas Journal of Animal Science, 2015. **28**(3): p. 343-350.
34. Tsai, W.T. and P.C. Huang, *Characterization of acid-leaching cocoa pod husk (CPH) and its resulting activated carbon*. Biomass Conversion and Biorefinery, 2018: p. 1-8.
35. Cruz, G., et al., *Production of activated carbon from cocoa (*Theobroma cacao*) pod husk*. Journal of Civil & Environmental Engineering, 2012. **2**(2): p. 1-6.

36. Yahya, M.A., Z. Al-Qodah, and C.W.Z. Ngah, *Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review*. Renewable and Sustainable Energy Reviews, 2015. **46**: p. 218-235.

37\*. Lin, C.S.K., et al., *Food waste as a valuable resource for the production of chemicals, materials and fuels. Current situation and global perspective*. Energy & Environmental Science, 2013. **6**(2): p. 426-464.

**Comprehensive review discussing current situation of food waste/biomass in worldwide and their potential application.**

38. Shakhes, J., et al., *Tobacco Residuals As Promising Lignocellulosic Materials For Pulp And Paper Industry*. BioResource, 2011. **6**(4): p. 4481-4493.

39. Judt, M., *Non-wood plant fibres, will there be a come-back in paper-making?* Industrial Crops and Products, 1993. **2**(1): p. 51-57.

40. Duku, M.H., S. Gu, and E.B. Hagan, *A comprehensive review of biomass resources and biofuels potential in Ghana*. Renewable and Sustainable Energy Reviews, 2011. **15**(1): p. 404-415.

41. Mussatto, S.I. and J.A. Teixeira, *Lignocellulose as raw material in fermentation processes*, in *Current research, technology and education topics in applied microbiology and microbial biotechnology*, A. Mendez-Vilas, Editor. 2010, Formatec Research Center. p. 897-907.

42. Thomsen, S.T., Z. Kádár, and J.E. Schmidt, *Compositional analysis and projected biofuel potentials from common West African agricultural residues*. Biomass and Bioenergy, 2014. **63**: p. 210-217.

43. Nazir, N., et al., *Optimization of Pre-treatment Process of Cocoa Pod Husk Using Various Chemical Solvents*. International Journal on Advanced Science Engineering Information Technology, 2016. **6**(3): p. 403-409.

44\*\*. Lancefield, C.S., et al., *Pre-treatment of lignocellulosic feedstocks using biorenewable alcohols: towards complete biomass valorisation*. Green Chemistry, 2017. **19**(1): p. 202-214.

**An interesting approach of lignocellulosic fractionation that leads to a lignin fraction which is believed to retain many of the original key structural features in the plant.**

45. nee' Nigam, P.S., N. Gupta, and A. Anthwal, *Biotechnology for Agro-Industrial Residues Utilisation. Chapter 2: Pre-treatment of Agro-Industrial Residues*. 2009, UK: Springer Science+Business Media.

46. Ramos, L.P., *The chemistry involved in the steam treatment of lignocellulosic materials*. Química Nova, 2003. **26**: p. 863-871.

47. Auxenfans, T., et al., *Understanding the structural and chemical changes of plant biomass following steam explosion pretreatment*. Biotechnology for Biofuels, 2017. **10**(1): p. 36.

48. Alemawor, F., et al., *Effect of Pleurotus ostreatus fermentation on cocoa pod husk composition: Influence of fermentation period and Mn<sup>2+</sup> supplementation on the fermentation process*. African Journal of Biotechnology, 2009. **8**(9): p. 1950-1958.

49. Chen, S., et al., *Biological pretreatment of lignocellulosics: potential, progress and challenges*. Biofuels, 2010. **1**(1): p. 177-199.

50. Zakeski, J., et al., *The Catalytic Valorization of Lignin for the Production of Renewable Chemicals*. Chemical Reviews, 2010. **110**(6): p. 3552-3599.

51. Viell, J., et al., *Is biomass fractionation by Organosolv-like processes economically viable? A conceptual design study*. Bioresource Technology, 2013. **150C**: p. 89-97.

52. Abdul Karim, A., et al., *Phenolic composition, antioxidant, anti-wrinkles and tyrosinase inhibitory activities of cocoa pod extract*. BMC Complementary and Alternative Medicine, 2014. **14**(1): p. 381.

53. Sharma, S.K., et al., *Utilization of Food Processing By-products as Dietary, Functional, and Novel Fiber: A Review*. Critical Reviews in Food Science and Nutrition, 2016. **56**(10): p. 1647-1661.

54. Sundarra, A.A. and T.V. Ranganathan, *A Review - Pectin from Agro and Industrial Waste*. International Journal of Applied Environmental Sciences, 2017. **12**(10): p. 1777-1801.

55. Vriesmann, L.C. and C.L. de Oliveira Petkowicz, *Cacao pod husks as a source of low-methoxyl, highly acetylated pectins able to gel in acidic media*. International Journal of Biological Macromolecules, 2017. **101**(Supplement C): p. 146-152.

56. Mierczyńska, J., J. Cybulski, and A. Zdunek, *Rheological and chemical properties of pectin enriched fractions from different sources extracted with citric acid*. Carbohydrate Polymers, 2017. **156**(Supplement C): p. 443-451.

57. Hutomo, G.S., A. Rahim, and S. Kadir, *Pectin Isolation from Dry Pod Husk Cocoa with Hydrochloride Acid*. International Journal of Current Microbiology and Applied Sciences, 2016. **5**(11): p. 751-756.

58. Vriesmann, L.C. and C.L.O. Petkowicz, *Highly acetylated pectin from cacao pod husks (Theobroma cacao L.) forms gel*. Food Hydrocolloids, 2013. **33**(1): p. 58-65.

59. Adi-Dako, O., et al., *Physicochemical and antimicrobial properties of cocoa pod husk pectin intended as a versatile pharmaceutical excipient and nutraceutical*. Journal of pharmaceutics, 2016. **2016**.

60. Vriesmann, L.C., R.F. Teófilo, and C. Lúcia de Oliveira Petkowicz, *Extraction and characterization of pectin from cacao pod husks (Theobroma cacao L.) with citric acid*. LWT - Food Science and Technology, 2012. **49**(1): p. 108-116.

61.\* Marsiglia-López, D., et al., *Computer-Aided Economic Evaluation of Pectin Extraction from Cocoa Pod Husk (Theobroma cacao L.)*. Contemporary Engineering Sciences, 2017. **10**(30): p. 1493-1500.

**One of the few studies on the economic evaluation of pectin extraction from cocoa pod husks.**

62. Bach Knudsen, K.E., *The nutritional significance of "dietary fibre" analysis*. Animal Feed Science and Technology, 2001. **90**(1): p. 3-20.

63. Amir, I.Z., H.S. Hanida, and A. Syafiq, *Development and physical analysis of high fiber bread incorporated with cocoa (Theobroma cacao sp. ) pod husk powder*. International Food Research Journal, 2013. **20**(3): p. 1301-1305.

64.\* Martínez-Cervera, S., et al., *Cocoa fibre and its application as a fat replacer in chocolate muffins*. LWT - Food Science and Technology, 2011. **44**(3): p. 729-736.

**A research article, which examines dietary fibre composition, antioxidant capacity and physico chemical properties of cocoa pod husks.**

65. Quiles, A., et al., *Fiber from fruit pomace: A review of applications in cereal-based products*. Food Reviews International, 2018. **34**(2): p. 162-181.

66. Kosseva, M.R., *Food Industry Wastes: Chapter 6. Functional Food and Nutraceuticals Derived from Food Industry Wastes*, ed. M.R. Kosseva and C. Webb. 2013, USA: Elsevier.

67. Martínez, R., et al., *Chemical, technological and in vitro antioxidant properties of cocoa (Theobroma cacao L.) co-products*. Food Research International, 2012. **49**(1): p. 39-45.

68.\* Valadez-Carmona, L., et al., *Effects of microwaves, hot air and freeze-drying on the phenolic compounds, antioxidant capacity, enzyme activity and microstructure of cacao pod husks (Theobroma cacao L.)*. Innovative Food Science & Emerging Technologies, 2017. **41**: p. 378-386.

**A research article that assesses the effect of drying on the phenolic content of cocoa pod husks**

69. Abdul, K.A., et al., *Efficacy of cocoa pod extract as antiwrinkle gel on human skin surface*. Journal of Cosmetic Dermatology, 2016. **15**: p. 283-295.

70. Valadez-Carmona, L., et al., *Valorization of cacao pod husk through supercritical fluid extraction of phenolic compounds*. The Journal of Supercritical Fluids, 2018. **131**: p. 99-105.