Bioresource Technology Reports 25 (2024) 101772

Contents lists available at ScienceDirect

Bioresource Technology Reports

journal homepage: www.sciencedirect.com/journal/bioresource-technology-reports

Life cycle assessment of Colombian cocoa pod husk transformation into value-added products

Ana María Tovar, Luis Fernando Valencia, Aída Luz Villa *

Environmental Catalysis Research Group, Chemical Engineering Department, Engineering Faculty, Universidad de Antioquia UdeA, Medellín, Colombia

ARTICLE INFO

Keywords:
Life cycle assessment
Cocoa pod husk
Biowaste
Activated carbon
Potassium hydroxide
Cellulose

ABSTRACT

Cocoa production is an important activity for the Colombian agro-industry; however, the production of dry cocoa beans generates agricultural residues as the shells known as cocoa pod husk (CPH), represent 65 to 75 % of the fruit's wet weight. In this contribution, the Life Cycle Assessment (LCA) was conducted on the use of Colombian CPH to obtain activated carbon, potassium hydroxide and cellulose; production of KOH showed the lowest environmental impact. It was found that electricity consumption during the transformation process emerges as the primary contributor in the impact evaluation, and the categories with the most significant impact are HTPc, FETP and METP. When solar drying was considered for CPH pretreatment instead of drying in an oven, the impact quantification significantly decreased up to 63 % to produce cellulose, 56 % for KOH and 32 % for activated carbon. The value-added products obtained exhibit favorable properties, making them suitable for various potential applications.

1. Introduction

Cocoa production in Colombia is one of the most important agro-industrial activity due to its direct impact in the social and economic development of smallholder farmers. It is estimated that approximately 65,000 cocoa farming families benefit from this activity (MADR, 2021), many of them located in vulnerable and post-conflict regions (Abbott et al., 2018). In 2022 the national production was 62,158 tons of cocoa beans, where the departments with the highest participation in the cocoa production were Santander (36.8 %), Arauca (16.9 %), Antioquia (8.3 %), Tolima (5.8 %), Huila (5.7 %) and Nariño (5.4 %) (Fedecacao, 2023). Colombia produces three types of cocoa; the Criollo variety is known for its finesse, pleasant flavor and exquisite aroma but with high susceptibility to pests and low productivity; the Forastero, on the other hand, offers lower quality in terms of aroma and flavor; the hybrid variety results from crossing different clones in order to improve quality and productivity. Cocoa crops are developed in regions situated between 0 and 1200 m above mean sea level with deep soils, good aeration, moisture retention and drainage, receiving annual rainfall ranging from 1500 to 2500 mm, with an optimal average temperature range of 22 °C to 30 °C (UGRA, 2020). The *Theobroma cocoa* L. (Cocoa) tree is a species of the Malvaceae family; botanically the cocoa is considered a berry-like fruit that consists of three main parts, the cocoa beans, the mucilage and the cocoa pod husk (CPH). When mature, the pod contains between 20 and 40 beans covered by the mucilaginous pulp (Vásquez et al., 2019). The CPH is the external part of the fruit and comprises three tissues named exocarp, mesocarp, and endocarp (Guevara, 2018); it represents between 65 and 75 % in wet weight of the fruit. It is estimated that approximately 559,422 tons of CPH were generated in Colombia in 2022, taking into account the national cocoa production yield for that year. The accumulation of CPH due to its open field disposal which corresponds to conventional practice in Colombia, could contain infested plant material, leading to pest and disease dissemination that favors the loss of the harvest and generate public health problems (Devi et al., 2017); furthermore, the anaerobic decomposition of CPH left on the ground generates methane and nitrous oxide contributing to global climate change (Ortiz-Rodríguez et al., 2016).

Activated carbon is very important for the chemical industry in the production of catalysts, adsorbents for heavy metals and organic pollutants, to store gas and desalinate media. Potassium hydroxide is a raw material used in many applications, to produce potassium and agricultural chemicals, soaps, detergents, drain cleaners, paints, and varnish removers, as an electrolyte in alkaline batteries, as a reagent in the chemical industry, in the food industry to adjust pH, as a thickening agent and as a stabilizer (Tessenderlo Chemie NV, 2001). Cellulose can be physically and chemically modified in different types and

* Corresponding author.
E-mail address: aida.villa@udea.edu.co (A.L. Villa).

https://doi.org/10.1016/j.biteb.2024.101772
Received 13 November 2023; Received in revised form 17 January 2024; Accepted 30 January 2024
Available online 2 February 2024

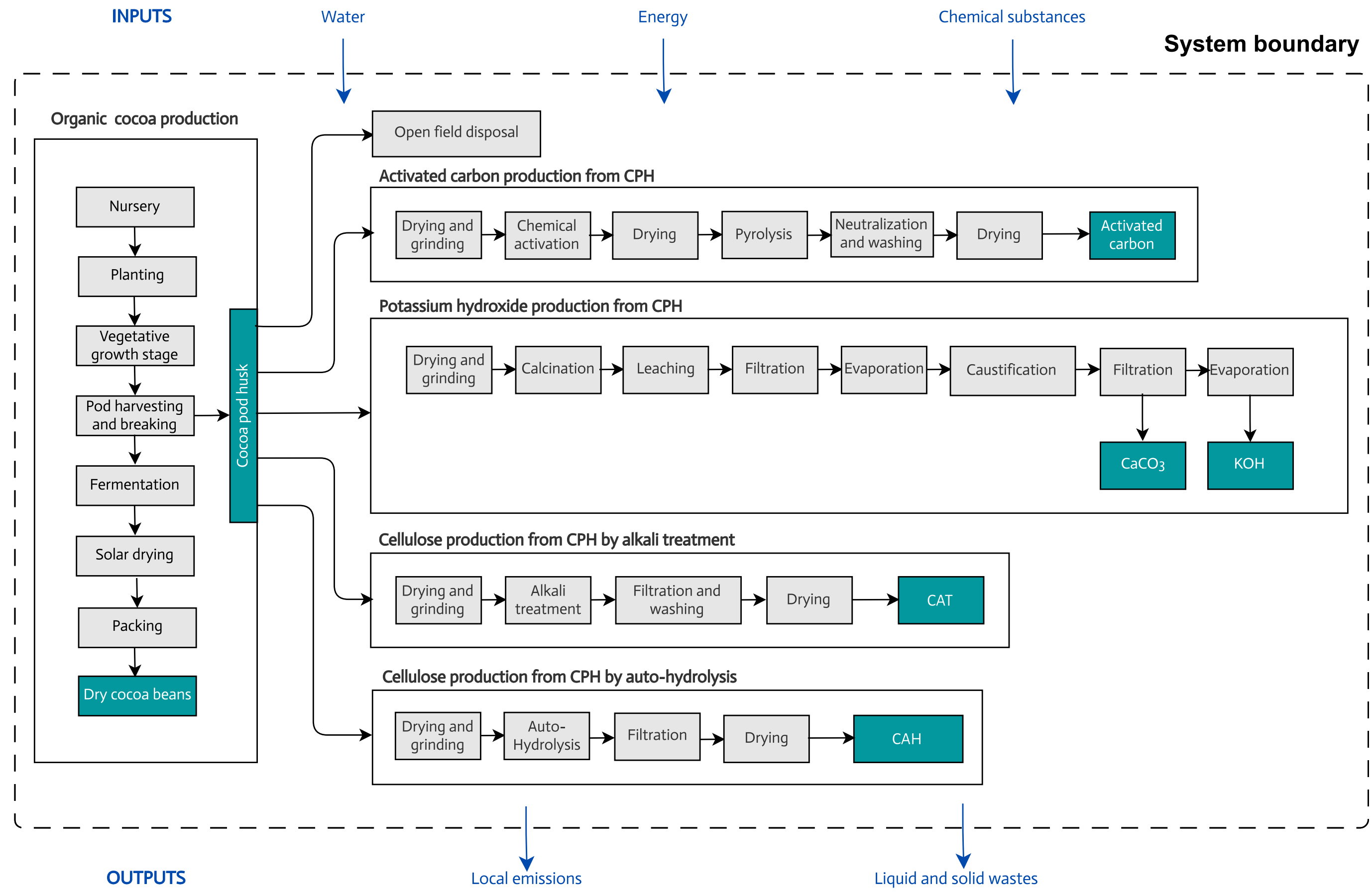

Fig. 1. System boundaries of products obtained from CPH for the LCA study.

Table 1
Midpoint impact categories and related characterization factors.

Impact category	CF_m	Unit
Climate change	Global warming potential (GWP)	kg CO_2-eq to air
Human toxicity: cancer	Human toxicity potential (HTPc)	kg 1.4-DCB-eq to urban air
Terrestrial acidification	Terrestrial acidification potential (TAP)	kg SO_2-eq to air
Freshwater eutrophication	Freshwater eutrophication potential (FEP)	kg P-eq to freshwater
Terrestrial ecotoxicity	Terrestrial ecotoxicity potential (TETP)	kg 1.4-DCB-eq to industrial soil
Freshwater ecotoxicity	Freshwater ecotoxicity potential (FETP)	kg 1.4-DCB-eq to freshwater
Marine ecotoxicity	Marine ecotoxicity potential (METP)	kg 1.4-DCB-eq to marine water
Water use	Water consumption potential (WCP)	m^3 water-eq consumed
Mineral resource scarcity	Surplus ore potential (SOP)	kg Cu-eq
Fossil resource scarcity	Fossil fuel potential (FFP)	kg oil-eq

configurations to be used in a wide range of applications in textiles, foods, biomedicals, hygiene, pharmaceutical, and cosmetics products, absorbent materials, paper and cardboard, paint, coating, and construction industries (Delucis et al., 2021).

CPH has been used as a raw material for obtaining a range of products, including activated carbon (Cruz, 2012; Eletta et al., 2020; Tejada et al., 2017; Tiegam et al., 2021), potassium hydroxide and carbonate (Afrane, 1992; Daniyan et al., 2014; Kone et al., 2020; Maliki et al., 2020), antioxidants (Campos-Vega et al., 2018; Sakagami et al., 2008), proteins (Serra Bonvehí and Ventura Coll, 1999), food fibers (Yapo et al., 2013), lignocellulosic components (Adeleye et al., 2022; Akinjokun et al., 2021; Torres, 2019), and pectin (Chan and Choo, 2013; Muñoz-Almagro et al., 2019), among others products. Additionally, investigations have explored its application in energy production through both thermochemical (Adjin-Tetteh et al., 2018; Dahunsi et al., 2019; Martínez et al., 2015) and biochemical (Antwi et al., 2019; Sandesh et al., 2020) conversion processes. These studies underscore the significant potential of this biowaste and its transformation into value-added products.

Considering that there are many ways for the utilization of CPH, the application of the Life Cycle Analysis (LCA) methodology serves as a valuable tool for assessing and comparing the environmental performance of these transformation processes for the utilization of this agro-industrial waste. The LCA methodology considers the guidelines of the standard ISO 14040 and consists of the determination and evaluation of the inputs, outputs and the potential environmental impacts of a product system or technologies throughout its life cycle (ICONTEC, 2007). The LCA enables the identification of critical points where optimization and/or substitutions are necessary to minimize the environmental impacts.

The LCA methodology was applied to the primary process of cocoa production in Colombia by Ortiz-R et al. (2014). This study evaluated the environmental performance of cocoa production using only the global warming potential (GWP) factor without including the post-harvest stage nor its wastes, identifying that in Colombia the farmers' agricultural practices are not homogeneous and the results of the LCA depends on them. The farm with the highest emission had 607 kgCO2-eq (per ha per year), where the use of synthetic fertilizers in high doses was the largest contributor to this environmental impact; and negative GWP values were observed for farms where improved practices such as

Table 2
Physicochemical characterization of CPH on dry matter basis for this study and other authors.

Parameter	Value[a]	Minimum	Maximum	References
Moisture, %	3.60	6.67	16.1	(Adjin-Tetteh et al., 2018; Forero-Nuñez et al., 2015; Nguyen and Nguyen, 2017; Orjuela et al., 2019; Syamsiro et al., 2011; Tiegam et al., 2021; Titiloye et al., 2013; Villamizar et al., 2017)
Volatile matter, %	72.9	49.9	74.1	(Adjin-Tetteh et al., 2018; Forero-Nuñez et al., 2015; Maleka, 2016; Orjuela et al., 2019; Syamsiro et al., 2011; Tiegam et al., 2021; Titiloye et al., 2013)
Ash, %	8.50	6.70	16.2	(Adjin-Tetteh et al., 2018; Forero-Nuñez et al., 2015; Nguyen and Nguyen, 2017; Orjuela et al., 2019; Syamsiro et al., 2011; Titiloye et al., 2013; Vásquez et al., 2019; Villamizar et al., 2017; Vriesmann et al., 2011)
Fixed carbon, %	15.0	10.4	20.5	(Adjin-Tetteh et al., 2018; Forero-Nuñez et al., 2015; Orjuela et al., 2019; Syamsiro et al., 2011; Titiloye et al., 2013)
Hemicellulose, %	52.1	9.00	37.0	(Daud et al., 2014; Vásquez et al., 2019)
Cellulose, %	23.7	15.1	35.4	(Daud et al., 2014; Grillo et al., 2019; Vásquez et al., 2019)
Lignin, %	16.5	14.7	21.4	(Daud et al., 2014; Vriesmann et al., 2011)
K, mg/100 g	2795	2716	3220	(Antwi et al., 2019; Vásquez et al., 2019; Vriesmann et al., 2011)

[a] The value corresponds to the average of three fruits from Criollo and Trinitario varieties that were analyzed for this study.

organic fertilization was used. The carbon footprint (CF) of the Colombian cocoa production was evaluated by Ortiz-Rodríguez et al. (2016) comparing agricultural practices under two scenarios: conventional and agroforestry managements. For the studied managements, the cocoa pod husk wastes left on the ground have a strong impact on CF due to the anaerobic decomposition of organic matter generating methane and nitrous oxide, which represent >85 % of emissions over the CF (Ortiz-Rodríguez et al., 2016). In Philippines, the entire system from agricultural activities until obtaining the cocoa dried beans was analyzed by LCA. The authors reported that pest management, nutrient management, transportation, and harvesting contributed the most to the negative environmental impact, and that the highest scoring category impact was for the climate change (Leyte et al., 2017). Tiegam et al. (2021) investigated benefits and environmental impacts of production of activated carbon from CPH at laboratory scale through LCA, involving the cocoa production, post harvesting stage and the transformation of CPH. The authors found that the electricity used in the transformation stage was the main contributor to the environmental impact (Tiegam et al., 2021). Recanati et al. (2018) evaluated the environmental impacts of an Italian dark chocolate through a holistic LCA; the authors reported that the upstream phase (cultivation and transportation) and energy supply at the manufacturing plant were the main contributors on the overall environmental impact. When CPH were considered as a co-product for producing value-added products and not as a biomass residue, there was a reduction of impacts ranging from 6.5 % for GWP to 12 % for the abiotic depletion category which corresponds to an environmental benefit (Recanati et al., 2018).

The main objective of this contribution is to use the LCA methodology to carry out the environmental assessment of the pod husk transformation of Colombian cocoa into valued-added products such as activated carbon (AC), potassium hydroxide (KOH), and cellulose. The LCA results allow identifying which of the evaluated transformation processes generates the least environmental impact for the use of CPH and determine if this utilization yields environmental benefits compared to the conventional disposal of this biowaste.

2. Material and methods

2.1. Organic cocoa production

CPH was obtained from organic cocoa production of the association "Héroes del cultivo" in the rural zone of San Bernardo-Ibagué (Colombia), located at an altitude of 1285 m above sea level with an average temperature of 28 °C. The cocoa crop begins in the nursery, where compost soil, sand, and seeds of the crops from the studied area are used for germination; one month later the tree is transplanted into the ground. During the vegetative growth stage, nutrient management, pest, weed, shadow, and shape control is carried out. Nutrient management is done with a "Héroes del cultivo" formulation of the Supermagro biofertilizer and lime. Pest, weed, shadow and shape control is done mechanically with chainsaw, and manually with hacksaw and pruner (R. Tapiero, personal interview, October 2022). The cocoa yield pattern was estimated based on field data collected during the first half of the year 2022, under the guidance of association's outstanding leader, Robinson Tapiero. This estimation considered only the first quality cocoa fruit (product). The harvesting and breaking of cocoa pods are done on the farm; the harvest is done manually with a special knife or pruner, and the breaking of pods is done with a blunt machete. The grains together with the mucilage are collected in plastic buckets to be taken to the benefit plant and CPH is left on the ground. At the benefit plant, the cocoa with mucilage ("cocoa in slime") is fermented in wooden bin for minimum 6 days, then it is dried in the sun in large wooden stretchers until the humidity of grains is reduced to around 7 %. Finally, the selected grains are packed in 50-kilogram jute bags and sealed with seams (R. Tapiero, personal interview, October 2022); most of this work in the benefit plant is manual.

2.2. Description of CPH transformation processes

CPH samples from Criollo and Trinitario varieties were analyzed. The pods were processed to determine their physicochemical properties. Thermogravimetric analysis (TGA) was carried out in nitrogen atmosphere using a TGA Q500 equipment. Moisture content was calculated using the constant weight of the sample after treatment at 107 °C (ISO 18134-3:2015); volatile matter content was measured as weight loss after treating the CPH at 900 °C for 10 min (ISO 18123:2015); the ashes content was evaluated with the residue after burning to a constant weight at 550 °C (ISO 18122:2015). For determining hemicellulose (Van Soest AOAC 2002.4), cellulose (Van Soest AOAC 973.18), and lignin (Van Soest H_2SO_4), first a digestion with acid detergent was performed to determine the hemicellulose content in the filtrate, then, the residue was digested with 72 % sulfuric acid to measure cellulose and lignin. Potassium content was determined by atomic absorption (SM 3111B) and the % fixed carbon was calculated using Eq. (1):

$$\%\text{Fixed carbon} = 100 - (\%\text{Volatile matter} + \%\text{Ashes} + \%\text{Moisture}) \quad (1)$$

The quantification and transformation processes were carried out with a 50–50 mixture of the Criollo and Trinitario varieties. The yield of

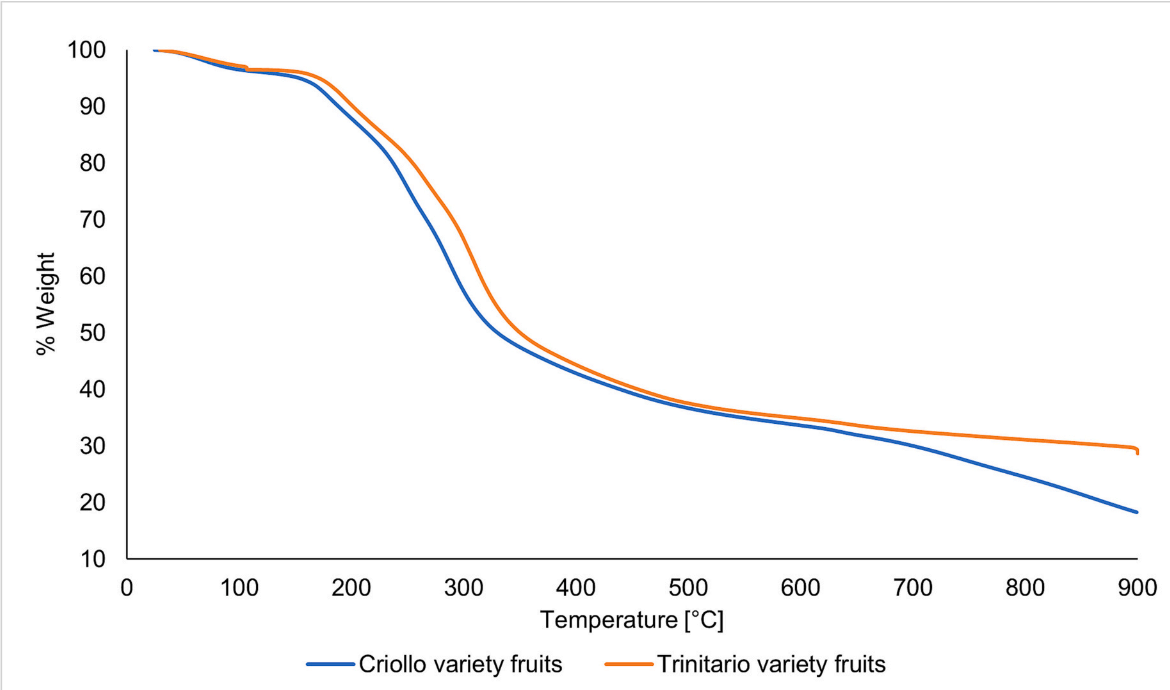

Fig. 2. TGA of analyzed CPH samples.

the obtained value-added products was determined using Eqs. (2) and (3):

$$\%\text{Yield on wet basis} = \frac{\text{mass of value} - \text{added product}}{\text{mass of CPH non} - \text{pretreated}} \times 100 \tag{2}$$

$$\%\text{Yield on dry basis} = \frac{\text{mass of value} - \text{added product}}{\text{mass of CPH pretreated (dried)}} \times 100 \tag{3}$$

2.2.1. *Activated carbon production from CPH*

CPH was dried and ground; the material with a particle size <90 μm was used for chemical activation with 85 % reagent grade potassium hydroxide (Merck), using a 1:2 (KOH:CPH) impregnation ratio, adding water at a weight ratio of 1:3 (KOH:CPH mixture to water). The impregnated CPH was dried at room temperature for 12 h and then at 80 °C for 5.5 h using an oven; then the dried material placed in a ceramic crucible was pyrolyzed in a furnace in nitrogen atmosphere for 3 h at 500°C (Cruz, 2012; Tsai et al., 2020). After the pyrolysis process, the obtained solid was washed with a 1 M HCl aqueous solution and then with distilled water (Tiegam et al., 2021); finally, the activated carbon was dried and sieved. The obtained activated carbon was characterized by SEM-EDX to semi quantitatively determination of its composition and analysis of its structure. Additionally, the textural properties of AC were evaluated with the isotherm. The adsorption-desorption analysis conducted using nitrogen as adsorbate in the Sortometer Micrometrics (ASAP 2020 PLUS).

2.2.2. *Potassium hydroxide production from CPH*

CPH with a particle size lower than 90 μm was placed in a ceramic crucible and calcined at 650 °C for 1 h in a furnace. During the calcination process, the potassium salts present in the CPH were oxidized to form potassium oxide which reacted with the carbon dioxide generated during calcination to produce potassium carbonate (Eq. (4)). At the same time, a small part of potassium carbonate reacted with water vapor to produce potassium hydroxide and bicarbonate (Eq. (5)) (Afrane, 1992; Olufemi et al., 2017).

$$K_2O\,(s) + CO_2(g) \rightarrow K_2CO_3(s) \tag{4}$$

$$K_2CO_3(s) + H_2O(g) \rightarrow KOH(s) + KHCO_3(s) \tag{5}$$

The ashes obtained that contained mainly K_2CO_3, were leached with water at a weight ratio of 1:10 (ash:water). The alkaline solution was allowed to cool and then filtered to obtain a clear extract containing K_2CO_3 and KOH; the extract was heated at 90 °C until the water was completely evaporated to obtain the solid product (Daniyan et al., 2014). By titration, the content of K_2CO_3 and KOH present in the obtained solid was determined. Then, a causticization process was carried out in an aqueous medium using calcium hydroxide (Merck) to produce KOH in solution and calcium carbonate as a precipitate (Ofori, 2017). The new cooled alkaline solution was filtered to obtain the extract that was heated at 90 °C until the water was completely evaporated for getting the solid material. The purity of potassium hydroxide was determined through acid-base titration using a reported double-indicator method. Initially, the phenolphthalein indicator was added to the aliquot and titrated with 0.1 M HCl. The change in color indicated the neutralization of all hydroxides and half of the carbonates. Subsequently, the titration was continued using methyl orange, and the change in color indicated the completion of the neutralization of the remaining half of the carbonates (Babayemi et al., 2010).

2.2.3. *Cellulose production from CPH*

Cellulose was obtained by two methodologies, one using an alkaline treatment and the other by autohydrolysis. Two cellulose products are obtained with different purity percentages and process yields, one is referred to as CAT (cellulose by alkaline treatment) and the other CAH (cellulose by autohydrolysis). The alkaline treatment was performed in a reflux system at 90 °C and 600 rpm for 2 h where CPH was treated with 2 % NaOH (PanReac) solution The obtained slurry was filtered with a vacuum equipment and the solid material was washed with distilled water until the alkali was removed (Adeleye et al., 2022); the product (CAT) was dried in an oven. For the autohydrolysis, distilled water was used with a solid:liquid ratio of 1:13 (pretreated CPH: distilled water) at 155 °C and at 1.5 MPa for 12 min in a cell pressurized with nitrogen. The slurry was then cooled at room temperature and filtered using vacuum equipment to obtain the hydrated solid product (CAH) that was dried in

Table 3
Life cycle inventory data result for transformation processes.

Item	Amount	Unit
Inventory data result of organic cocoa production		
Input		
Supermagro	14	L/ha
Lime	146.7	kg//ha
Gasoil	44	L/ha
Jute bag	1.1	kg/ha
Water rain	77,500	m^3/ha
Output		
Dry cocoa beans	117	kg/year.ha
Cocoa pod husk	1214	kg/year.ha
Mucilage	332	kg/year.ha
Local emissions		
Inventory data result to produce activated carbon from CPH		
Input		
Cocoa pod husk	42.8	g
Potassium hydroxide (KOH) 100 %	3.3	g
Hydrochloric acid (HCl) 30 %	4.2	mL
Deionized water	92.8	mL
Nitrogen	18	L
Electricity	6.3	kWh
Output		
Activated carbon	1.55	g
Liquid waste	71.5	mL
Local emissions		
Inventory data result to produce KOH from CPH		
Input		
Cocoa pod husk	178	g
Deionized water	51	mL
$Ca(OH)_2$	0.54	g
Electricity	3.6	kWh
Output		
Potassium hydroxide (85 %)	1.3	g
$CaCO_3$	1.2	g
Solid waste	0.9	g
Local emissions		
Inventory data result of CPH transformation to CAT		
Input		
Cocoa pod husk	71.2	g
Sodium hydroxide (NaOH) 50 %	8	g
Deionized water	398.6	mL
Electricity	3.4	kWh
Output		
Cellulose (85 % purity)	3.2	g
Liquid waste	412.5	mL
Local emissions		
Inventory data result of CPH transformation to CAH		
Input		
Cocoa pod husk	71.2	g
Deionized water	130	mL
Electricity	3.2	kWh
Output		
Cellulose (63.5 % purity)	6.2	g
Liquid waste	100	mL
Local emissions		

an oven at 80 °C (Torres, 2019). The α-cellulose content of obtained products was determined using the TAPPI T 203 standard.

2.3. *Life cycle assessment study*

The LCA methodology comprising four phases (ICONTEC, 2007). The first consists in establish the goal and scope definition, which provides the outline and guidance for the study; the second step is the inventory analysis where the consumption of resources and generation of emissions, wastes and energy for the analyzed system are estimated; this phase identifies the inventory flows and quantifies them, based on multiple data sources. In the third phase, the Life Cycle Impacts Assessment (LCIA) is carried out; LCIA aims to evaluate the magnitude and significance of the potential environmental impacts associated with impact categories and category indicators. Finally, in the interpretation phase the results of the two previous phases are evaluated according to the defined goal and scope to get the respective conclusions and recommendations (ICONTEC, 2007).

2.3.1. *Goal and scope definition*

The aim of this study was to assess the environmental performance of transformation of CPH obtained from organic cocoa cultivated in Ibagué (Colombia), to produce potassium hydroxide, activated carbon and cellulose. This work adopts a cradle-to-gate approach, encompassing the extraction of the main raw material (CPH) until obtaining the value-added products. The environmental impacts associated to organic cocoa production and CPH generation were evaluated and incorporated into the inventory of the subsequent CPH transformation processes to produce potassium hydroxide, activated carbon and cellulose. The scenario where the CPH is disposed of in an open field is also assessed. The systems under consideration exclude distribution, use or consumption, final disposal, or related transportation. The system boundary and process flows are shown in Fig. 1.

The functional unit (FU) chosen was 1 kg of CPH (wet weight) to evaluate the environmental impact of each transformation process to obtain value-added products (potassium hydroxide, activated carbon and cellulose). The same functional unit was used to determine the environmental impact of the CPH disposal in the open field.

Data sources include primary data collected through a field survey of cocoa farmers carried out between April to October 2022 in the rural zone of San Bernardo-Ibagué to assess the organic cocoa production. Additionally, laboratory tests were undertaken to obtain mass and energy balances and waste generation of transformation process to produce activated carbon, potassium hydroxide and cellulose from CPH. Secondary data obtained from Eco-invent 3.8 and Agri-footprint 6 database were gathered for support this research.

The LCA was performed with the SimaPro software version 9.4.0.2, the Ecoinvent 3.8 and Agri-footprint 6 databases, and the ReCiPe Midpoint (H) method for impacts assessment (Huijbregts et al., 2017). This study included 10 Midpoint indicators listed in ReCiPe2016. Attributional analysis was applied, and the allocation was conducted on a mass basis.

2.3.2. *Life cycle inventory analysis*

The inventory analysis includes interrelated inputs, such as raw materials from the technosphere, resources from the natural environment, and energy sources; furthermore, outputs such as final products, co-products, emissions, and waste materials are also considered. Within the defined system boundary, the life cycle inventory analysis for each system is constructed utilizing a combination of primary and secondary data sources, as outlined in the goal and scope definition.

2.3.3. *Life cycle impact assessment (LCIA) and Interpretation*

To quantify the potential environmental impact of each product, the ReCiPe Midpoint (H) method was used as the life cycle impact assessment. The hierarchical (H) perspective with midpoint ponderation is chosen by default, mainly because the values selected (Huijbregts et al., 2017) by this version are widely accepted in scientific and political contexts (ecoRaee, 2013). The midpoint impact category defined by the ReCipe 2016 (Huijbregts et al., 2017), and the evaluated characterization factors (CF_m) are listed in Table 1.

In the interpretation, the environmental performance in the production of activated carbon, potassium hydroxide and cellulose from CPH is determined, and the source of the environmental issue for each of the analyzed transformation processes of CPH is identified; and alternatives are proposed for the environmental improvement of the CPH transformation.

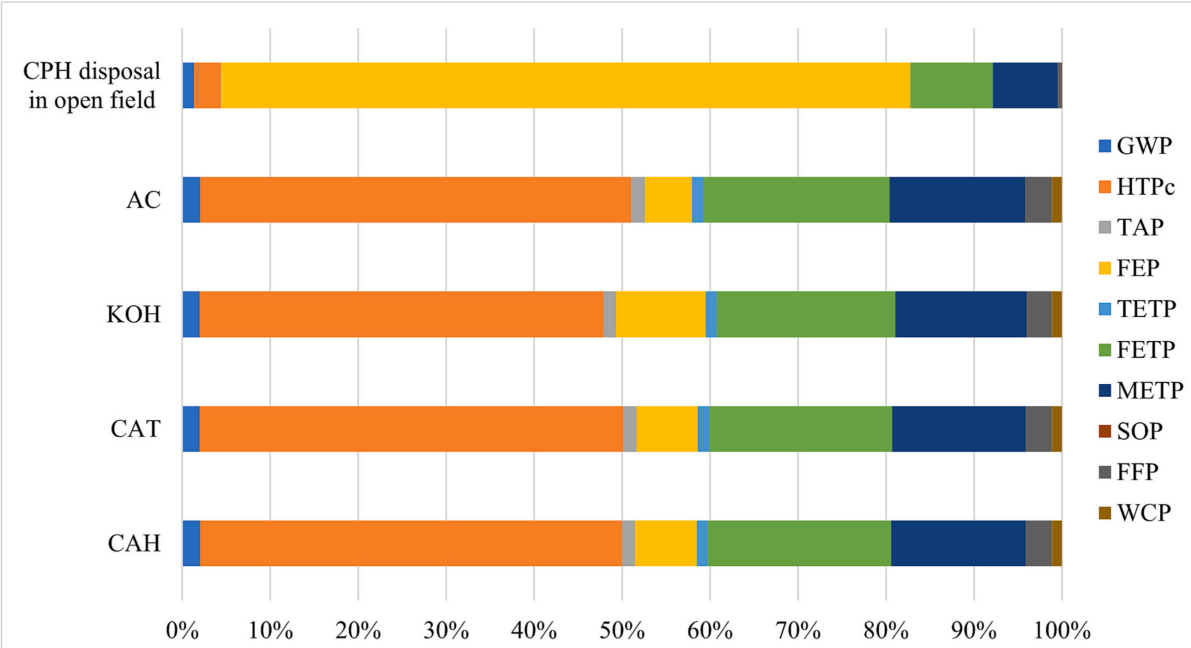

Fig. 3. Comparative impact assessment (normalized) of value-added products and CPH disposal in open field.

Table 4
Comparative life cycle impact assessment (characterization).

Impact category (CF_m)	Unit	AC	CAT	CAH	KOH	CPH disposal in open field
Normalized total score		0.173	0.058	0.053	0.013	0.011
Global warming potential (GWP)	kg CO2 eq	27.6895	9.1329	8.5377	2.0074	1.1577
Human toxicity potential: cancer (HTPc)	kg 1,4-DCB	0.8738	0.2862	0.2622	0.0601	0.0034
Terrestrial acidification potential (TAP)	kg SO2 eq	0.1071	0.0348	0.0326	0.0075	0.0003
Freshwater eutrophication potential (FEP)	kg P eq	0.0060	0.0026	0.0024	0.0008	0.0056
Terrestrial ecotoxicity potential (TETP)	kg 1,4-DCB	35.0847	11.3335	10.1925	2.3620	0.1799
Freshwater ecotoxicity potential (FETP)	kg 1,4-DCB	0.9202	0.3015	0.2790	0.0652	0.0257
Marine ecotoxicity potential (METP)	kg 1,4-DCB	1.1624	0.3813	0.3524	0.0825	0.0352
Mineral resource scarcity (SOP)	kg Cu eq	0.0312	0.0102	0.0092	0.0021	0.0002
Fossil resource scarcity (FFP)	kg oil eq	5.0596	1.6664	1.5475	0.3629	0.0454
Water consumption (WCP)	m^3	0.5360	0.1787	0.1628	0.0375	0.0009

3. Results and discussions

3.1. Cocoa pod husk analysis

The analysis of cocoa fruits show that the ratio of CPH generated to the dry cocoa beans produced is approximately 10:1 (CPH:dried cocoa beans). The physicochemical characterization of CPH on a dry matter basis is summarized in Table 2 and compared with reported values. Furthermore, the TGA analysis is shown in Fig. 2.

The results obtained for most of the parameters fall within the ranges previously reported by other authors; the differences could be associated to climate, storage conditions, and location variations. The outcome reveals the promising potential of CPH obtained from agroforestry farms of the association "Héroes del cultivo" in the rural zone of San Bernardo-Ibagué (Colombia) to produce activated carbon, potassium hydroxide and cellulose.

3.2. Life cycle inventory analysis result

The number and quantity of inputs and outputs related to the raw materials, resources, energy, products, co-products, and waste for each system are detailed in Table 3. Lime and Supermagro biofertilizer are the primary materials for growing organic cocoa. Regarding the outcomes, the CPH is the main output of this system and the CPH:dry cocoa beans ratio stands at 10:1. The yield to produce activated carbon, potassium hydroxide, cellulose unbleached by alkaline treatment and cellulose unbleached by autohydrolysis, from non-pretreated CPH (wet basis), are 3.6 %, 0.73 %, 4.5 % and 8.7 %, respectively.

3.3. Comparative life cycle impact assessment

Fig. 3 illustrates the overall environmental impacts (normalized) of value-added products obtained from CPH, as along with the disposal of CPH in an open field. The normalized total scores of life cycle impact assessment for each evaluated scenario, ranked in order of the greatest environmental impact are: 0.173 to produce AC, 0.058 to produce CAT, 0.053 to produce CAH, 0.013 to produce KOH, and 0.011 for the disposal of CPH in an open field. The results show that for the scenario where CPH is disposed of in an open field, the highest impact value corresponds to FEP (78.4 %). This is attributed to the degradation of the large amount of biomass, resulting in the generation of leachates that end up in bodies of water, leading to adverse effects including eutrophication and ecotoxicity (Güereca et al., 2006).

For the transformation processes of CPH, the categories with the most significant impact are HTPc, FETP and METP. In the production of activated carbon, HTPc accounts for 49.1 %, FETP for 21.1 %, and METP for 15.5 %. To produce KOH, the contributions are 45.9 % (HTPc), 20.3 % (FETP), and 14.9 % (METP). Similarly, to cellulose production using

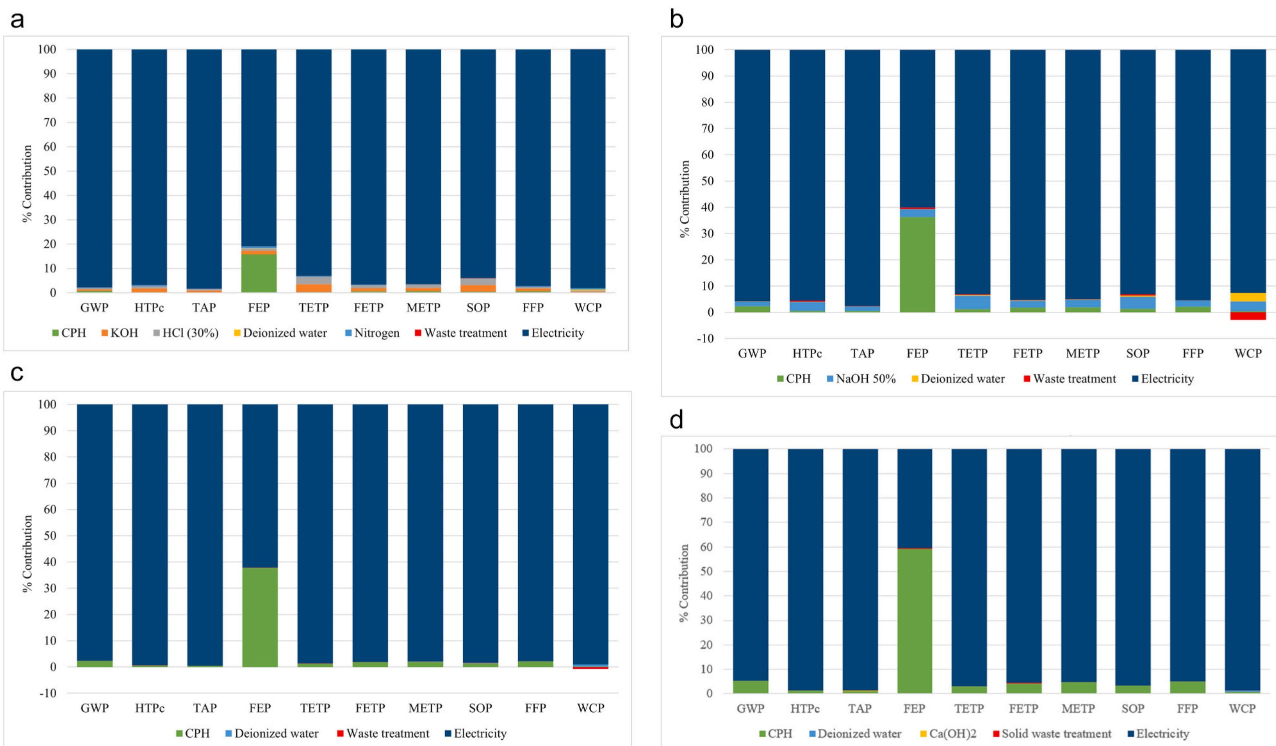

Fig. 4. Impact contribution by transformation processes to produce AC (a), CAT (b), CAH (c), KOH (d).

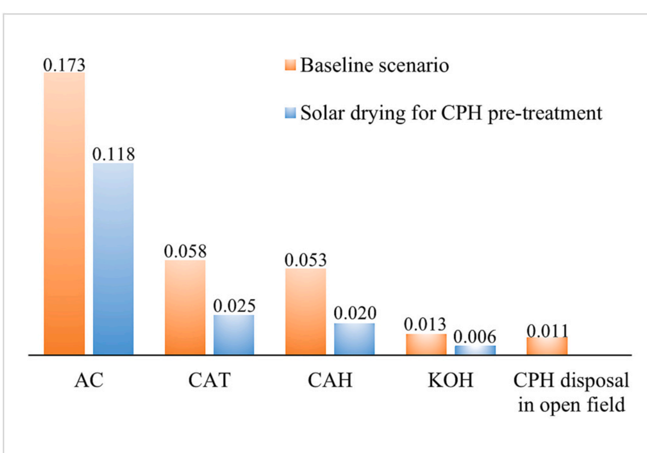

Fig. 5. Sensitivity analysis by transformation processes.

either of the two methodologies, the percentages are 48.1 % (HTPc), 20.9 % (FETP), and 15.3 % (METP). Minor impact is noticeable in the FEP category, accounting 10.2 % to produce KOH, 7 % to produce cellulose and 5.4 % to produce activated carbon. FFP registers a modest 3 % of impact, followed by GWP at 2 %, TAP at 1.5 %, TETP at 1.3 % and WCP at 1.2 % across all transformation processes. Finally, SOP category has a negligible contribution to the overall environmental assessment.

Table 4 presents the characterization of life cycle impact assessment for the evaluated processes. The results reveal that among the transformation processes to use CPH, the production of KOH exhibits the most favorable environmental performance.

3.4. *Impact contributions for CPH transformation processes*

The impact contribution analysis allows to identify the hotspots of the environmental assessment for each of the analyzed transformation processes of CPH and propose alternatives for environmental improvement of the processes. The impact contribution of the CPH transformation processes is shown in Fig. 4a, b, c and d. It is observed that for all transformation processes the electricity consumption is the most significant contribution factor across all evaluated CF_m. Electricity exceeds values of 90 % for most categories, with the exceptions of the FEP category in each transformation process. The CPH becomes a notable contributor in FEP category to produce activated carbon (15.8 %), cellulose by alkaline treatment (36.3 %), cellulose by autohydrolysis (37.7 %) and KOH (59.3 %). This contribution can be associated to the nutrients and minerals that eventually end up in water bodies during cocoa production where the CPH is generated.

For all transformation processes, the oven-drying stage of the CPH pre-treatment stands out as the largest contributor to the overall energy requirement of each process. Additionally, the other drying stages throughout the transformation process play an important role in augmenting the energy demand. Another significant energy-intensive stage within transformation processes is the pyrolysis performed at 500 °C for 3 h to produce activated carbon. To produce cellulose through alkaline treatment, a positive contribution to the environment is observed in the WCP category. Here, a 2.9 % debit emerges from waste treatment, which corresponds to the recovery of water during the liquid waste treatment process. The effect is also observed but to a lesser extent (0.8 % debit) in the production of cellulose by autohydrolysis because the amount of recovered water is lower.

The use of reagents does not significantly contribute to any of the assessed impacts for any of the transformation processes, probably because a few numbers of reagents are used, they are non-toxic and are used in small quantities.

3.5. *Sensitivity analysis*

Given that the energy requirement significantly influences the LCA result of all evaluated transformation processes, a sensitivity analysis was conducted to evaluate the effects of a different type of energy

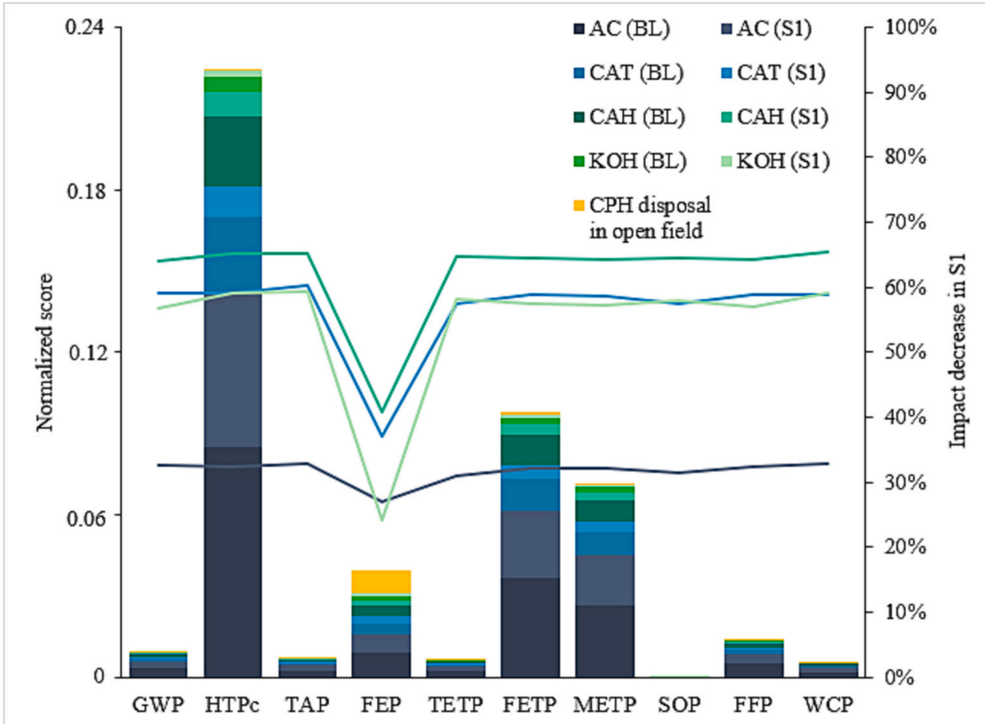

Fig. 6. Normalized score and percentage decrease from sensitivity analysis. The columns represent the normalized score for each product and scenario. The solid line represents the impact decrease in S1 with respect to BL.

Table 5
Comparison of yields (dry basis) obtained in this study with reported values.

Product	% Yield	Reference
AC	21.0	(Cruz, 2012)
	30.0	(Adjin-Tetteh et al., 2018)
	35.5	(Tsai et al., 2018)
	42.3	(Adeleye et al., 2022)
	24.9	(This study)
CAT	31.0	(Ordu et al., 2011)
	35.0	(Norasikin et al., 2022)
	42.3	(Adeleye et al., 2022)
	48.5	(Ogunneye et al., 2020)
	31.0	(This study)
CAH	63.0	(Torres, 2019)
	60.1	(This study)
KOH	1.57	(Ofori, 2017)
	5.91	(Kamalu, 2005)
	5.00	(This study)

Table 6
Structural properties of activated carbon.

Property	
BET surface area (m^2/g)[a]	467.5
Micropore surface area (m^2/g)[b]	370.7
Total pore volume (cm^3/g)[c]	0.23
Micropore volume (cm^3/g)[d]	0.14
Pore Width (nm)[b]	1.09

[a] BET surface area based on the relative pressure (P/P_0) ranging from 0.05 to 0.4.
[b] Estimated by t-plot method.
[c] Total pore volume obtained at relative pressure of about 0.99.
[d] Micropore volume by t-plot method.

source. The baseline (BL) scenario corresponds to the outcomes discussed in Section 3.2, and it is compared with the alternative (S1) of using solar energy for the CPH drying in the pre-treatment step instead of utilizing an oven, which is technically feasible although the process takes more time. This corresponds to a reduction of 2.1 kWh of electricity in all inventory analyses for each of the transformation processes.

Fig. 5 shows the reduction in normalized total score of overall environmental assessment for each transformation process when solar drying is used in the CPH pretreatment stage. The highest reduction percentage is obtained in the production of cellulose by autohydrolysis (62.3 %), followed by the production of cellulose through alkaline treatment (56.9 %), KOH production (53.8 %) and finally the activated carbon production (31.8 %). The LCIA using solar drying for CPH pretreatment reveals that producing KOH using CPH generates a lesser impact compared with the conventional practice of disposing this biowaste in an open field. This outcome is also a result of calcium carbonate being obtained as a co-product during the production of potassium hydroxide, with the impact allocation percentage distributed between the two products: 52 % for KOH and 48 % for $CaCO_3$.

Examining the result by impact category it is observed that the same trends persist across all products assessed under both, the baseline scenario, and the alternative scenario (S1). Fig. 6 shows that the categories with the most significant impact (normalized score) are HTPc, FETP, and METP; the FEP category exhibits a notable impact; the FFP, GWP, TAP, TETP, and WCP categories show a minor impact, and the SOP category shows a negligible impact. The percentage reduction in impact (solid line in Fig. 6) for scenario S1 remains consistent on average across all categories to produce activated carbon. For CAT, CAH, and KOH, it is identified that the optimization in the use of conventional energy affects the evaluated categories differently, since the decrease in the FEP category is considerably smaller compared to the others. Furthermore, it is observed that the CPH disposal in open field has the highest score within the same category (FEP), which validates the previous analysis presented in Section 3.3. This reinforces the finding that CPH plays a pivotal role in contributing to the FEP impact.

The opportunity to optimize the transformation processes utilized in this study is identified with the aim of reducing the energy requirements for each process. Furthermore, it would be beneficial to explore alternative technologies for transformation, assessing their viability for industrial-scale production and considering the integration of renewable energy sources to determine their potential to improve the environmental performance.

3.6. Characteristics of value-added products obtained from CPH

In relation to the pretreated CPH (which is dried and ground), the yield significantly increases because the high moisture content present in the CPH is eliminated during the first drying stage. The yield to produce AC, CAT, CAH, and KOH from CPH pretreated (dry basis) are 24.9 %, 31.0 %, 60.1 % and 5.0 % respectively. These results are comparable with those reported in previous studies under similar process conditions (see Table 5).

SEM-EDX semiquantitative analysis of obtained activated carbon indicated that the material contains mainly carbon (89 %), oxygen (7.8 %), Mg (0.7 %), Cl (1.0 %), and K (1.5 %). The high content of carbon is mainly attributed to the lignocellulosic composition and the efficiency in the carbonization process, being higher than those obtained in similar studies: 72.9 % and 60.7 % reported by Cruz (2012) and Tejada et al. (2017), respectively. The obtained structural properties (see Table 6) are like those observed in previous studies that utilized KOH as an activator and CPH as a carbon source. Previously reported BET surface area are 490 m^2/g at 800 °C carbonization temperature (Cruz, 2012), and 484 m^2/g at 500 °C carbonization temperature (Tsai et al., 2018). The findings in the Table 6 indicate that the porosity of the activated carbon is predominantly characterized by micropores, accounting for 79.3 % of the surface area and 62.6 % of the total volume. The characteristics of the obtained AC show a great potential as an adsorbent material for contaminants in aqueous medium. This material is especially effective for the removal of heavy metals, ink, and certain pharmaceutical active compounds such as amoxicillin (Eletta et al., 2020).

The unbleached α-cellulose content was determined, resulting in purities of 85 % and 63.5 % for the product obtained through alkaline treatment and autohydrolysis, respectively. This is consistent with the results of a similar study conducted by Torres (2019). The obtained α-cellulose content implies that CPH has potential as a non-wood fiber for use in pulp and paper production (Torres, 2019).

The potassium hydroxide content indicates a purity of 84.16 % of KOH obtained from CPH. The reported purity of commercial KOH by the provider (MERCK, Reference 221,473, ACS reagent, ≥85 % pellets) is stated as being ≥85 %. These results highlight the effectivity of the used process for obtaining KOH using CPH as a source of potassium to produce agricultural chemicals, soaps, detergents, drain cleaners, paint, and varnish removers, as an electrolyte in alkaline batteries, as a reagent in the chemical industry (Tessenderlo Chemie NV, 2001).

4. Conclusion

The outcome of this study suggests that the production of KOH exhibits the highest environmental performance to use the CPH, followed by cellulose obtained through autohydrolysis, cellulose obtained through alkaline treatment, and finally activated carbon. Across all transformation processes, it becomes evident that electricity consumption during the transformation process emerging as the primary contributor to the LCA results for almost all impact categories, and that the categories with the most significant impact are HTPc, FETP and METP. Additionally, the CPH itself plays a significant role in the Freshwater Eutrophication Potential impact (FEP). The sensitivity analysis shows that optimizing energy usage leads to a significant reduction in the total environmental impact assessment for each product obtained from CPH. It also highlights that the production of KOH has the lowest environmental impact when compared to the conventional disposal of CPH in open field. The characterization of the products obtained from CPH shows that potassium hydroxide, cellulose and activated carbon have favorable properties, making them suitable for various potential applications.

CRediT authorship contribution statement

Ana María Tovar: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Luis Fernando Valencia:** Visualization, Methodology, Investigation. **Aída Luz Villa:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgements

The authors thank financial support from Universidad de Antioquia and the Ministry of Science, Technology and Innovation, the Ministry of Education, the Ministry of Industry, Commerce and Tourism, and ICETEX, Programme Ecosistema Científico-Colombia Científica, from the Francisco José de Caldas Fund, Grant RC-FP44842-212-2018.

References

Abbott, P.C., Benjamin, T.J., Burniske, G.R., Croft, M.M., Fenton, M., Kelly, C.R., Lundy, M., Rodriguez Camayo, F., Wilcox Jr., M.D., 2018. An Analysis of the Supply Chain of Cacao in Colombia (Cali).

Adeleye, O.A., Bamiro, O.A., Albalawi, D.A., Alotaibi, A.S., Iqbal, H., Sanyaolu, S., Femi-Oyewo, M.N., Sodeinde, K.O., Yahaya, Z.S., Thiripuranathar, G., Menaa, F., 2022. Characterizations of alpha-cellulose and microcrystalline cellulose isolated from cocoa pod husk as a potential pharmaceutical excipient. Materials (Basel) 15, 5992. https://doi.org/10.3390/MA15175992.

Adjin-Tetteh, M., Asiedu, N., Dodoo-Arhin, D., Karam, A., Amaniampong, P.N., 2018. Thermochemical conversion and characterization of cocoa pod husks a potential agricultural waste from Ghana. Ind. Crop. Prod. 119, 304–312. https://doi.org/10.1016/J.INDCROP.2018.02.060.

Afrane, G., 1992. Leaching of caustic potash from cocoa husk ash. Bioresour. Technol. 41 https://doi.org/10.1016/0960-8524(92)90177-Y.

Akinjokun, A.I., Petrik, L.F., Ogunfowokan, A.O., Ajao, J., Ojumu, T.V., 2021. Isolation and characterization of nanocrystalline cellulose from cocoa pod husk (CPH) biomass wastes. Heliyon 7. https://doi.org/10.1016/J.HELIYON.2021.E06680.

Antwi, E., Engler, N., Nelles, M., Schüch, A., 2019. Anaerobic digestion and the effect of hydrothermal pretreatment on the biogas yield of cocoa pods residues. Waste Manag. 88, 131–140. https://doi.org/10.1016/J.WASMAN.2019.03.034.

Babayemi, J.O., Dauda, K.T., Nwude, D.O., Kayode, A.A.A., 2010. Evaluation of the composition and chemistry of ash and potash from various plant materials - a review. J. Appl. Sci. https://doi.org/10.3923/jas.2010.1820.1824.

Campos-Vega, R., Nieto-Figueroa, K.H., Oomah, B.D., 2018. Cocoa (*Theobroma cacao* L.) pod husk: renewable source of bioactive compounds. Trends Food Sci. Technol. https://doi.org/10.1016/j.tifs.2018.09.022.

Chan, S.Y., Choo, W.S., 2013. Effect of extraction conditions on the yield and chemical properties of pectin from cocoa husks. Food Chem. 141 https://doi.org/10.1016/j.foodchem.2013.06.097.

Cruz, G., 2012. Production of activated Carbon from cocoa (*Theobroma cacao*) pod husk. J. Civ. Environ. Eng. 02 https://doi.org/10.4172/2165-784x.1000109.

Dahunsi, S.O., Adesulu-Dahunsi, A.T., Izebere, J.O., 2019. Cleaner energy through liquefaction of cocoa (*Theobroma cacao*) pod husk: pretreatment and process optimization. J. Clean. Prod. 226 https://doi.org/10.1016/j.jclepro.2019.04.112.

Daniyan, I.A., Adeodu, A.O., Adewumi, D.F., 2014. Design of a processor for the production of 30,000 tons of caustic potash per anum from cocoa pod husk. Int. J. Sci. Res. 2319.

Daud, Z., Awang, H., Mohd Kassim, A.S., Mohd Hatta, M.Z., Mohd Aripin, A., 2014. Cacao pod husk and corn stalk: alternative paper fibres study on chemical characterization and morphological structures. Adv. Mater. Res. 911, 331–335.

Delucis, R. de A., de Cademartori, P.H.G., Fajardo, A.R., Amico, S.C., 2021. Cellulose and its derivatives: properties and applications. Polysaccharides 221–252. https://doi.org/10.1002/9781119711414.CH11.

Devi, S., Gupta, C., Jat, S.L., Parmar, M.S., 2017. Crop residue recycling for economic and environmental sustainability: the case of India. Open Agric. 2, 486–494. https://doi.org/10.1515/OPAG-2017-0053.

ecoRaee, 2013. Informe de resultados del ACV. Universidad de Vigo. energylab. revertia.

Eletta, O.A.A., Adeniyi, A.G., Ighalo, J.O., Onifade, D.V., Ayandele, F.O., 2020. Valorisation of Cocoa (*Theobroma cacao*) pod husk as precursors for the production of adsorbents for water treatment. Environ. Technol. Rev. https://doi.org/10.1080/21622515.2020.1730983.

Fedecacao, 2023. Producción cacaotera presentó una reducción del 10% en 2022 por lluvias [WWW Document]. URL. https://www.fedecacao.com.co/post/producci%C3%B3n-cacaotera-present%C3%B3-una-reducci%C3%B3n-del-10-en-2022-por-lluvias (accessed 4.23.23).

Forero-Nuñez, C.A., Jochum, J., Vargas, F.E.S., 2015. Effect of particle size and addition of cacao pod husk on the properties of sawdust and coal pellets. Ing. Investig. 35, 17–23.

Grillo, G., Boffa, L., Binello, A., Mantegna, S., Cravotto, G., Chemat, F., Dizhbite, T., Lauberte, L., Telysheva, G., 2019. Analytical dataset of Ecuadorian cocoa shells and beans. Data Brief 22, 56–64. https://doi.org/10.1016/J.DIB.2018.11.129.

Güereca, L.P., Gassó, S., Baldasano, J.M., Jiménez-Guerrero, P., 2006. Life cycle assessment of two biowaste management systems for Barcelona, Spain. Resour. Conserv. Recycl. 49 https://doi.org/10.1016/j.resconrec.2006.03.009.

Guevara, J., 2018. The Chocolate Fruit: Looking Inside a Cacao Pod [WWW Document]. Perfect daily grind.

Huijbregts, M.A.J., Steinmann, Z.J.N., Elshout, P.M.F., Stam, G., Verones, F., Vieira, M., Zijp, M., Hollander, A., van Zelm, R., 2017. ReCiPe2016: a harmonised life cycle impact assessment method at midpoint and endpoint level. Int. J. Life Cycle Assess. 22, 138–147. https://doi.org/10.1007/S11367-016-1246-Y.

ICONTEC, 2007. Gestión Ambiental. Análisis de ciclo de Vida. Principios y Marco de Referencia. NTC-ISO 14040.

Kamalu, C., 2005. Production of Caustic Potash From Cocoa Pod Husk, vol. 4. NJISS.

Kone, K., Akueson, K., Norval, G., 2020. On the production of potassium carbonate from cacao pod husks. Recycling 5.

Leyte, J.E., Pacardo, E.P., Rebancos, C.M., Protacio, C.M., Alcantara, A.J., 2017. Environmental performance of Cacao (*Theobroma cacao* L.) production and primary processing. Philipp. J. Crop Sci. 42, 51–58.

MADR, 2021. Cadena de Cacao. Dirección de Cadenas Agrícolas y Forestales.

Maleka, D., 2016. Assessment of the Implementation of Alternative Process Technologies for Rural Heat and Power Production From Cocoa Pod Husks (Master of Science Thesis). KTH School of Industrial Engineering and Management, Stockholm.

Maliki, M., Ifijen, I.H., Omorogbe, S.O., 2020. Cocoa husks: a sustainable resource for alkali production. Int. J. Biol. Chem. Sci. 14, 2652–2658. https://doi.org/10.4314/ijbcs.v14i7.23.

Martínez, J.D., Villamizar, R.A., Ortíz, O.O., 2015. Characterization and evaluation of cocoa (*Theobroma cacao* L.) pod husk as a renewable energy source. Agrociencia 49, 329–345.

Muñoz-Almagro, N., Valadez-Carmona, L., Mendiola, J.A., Ibáñez, E., Villamiel, M., 2019. Structural characterisation of pectin obtained from cacao pod husk. Comparison of conventional and subcritical water extraction. Carbohydr. Polym. 217, 69–78. https://doi.org/10.1016/J.CARBPOL.2019.04.040.

Nguyen, V.T., Nguyen, N.H., 2017. Proximate composition, extraction, and purification of theobromine from cacao pod husk (*Theobroma Cacao* L.). Technologies (Basel) 5, 14. https://doi.org/10.3390/TECHNOLOGIES5020014.

Norasikin, H., Sariah, S., Eng, H.S., Mariani, R., 2022. Synthesis of Carboxymethyl Cellulose (CMC) from cocoa pod husk. In: AIP Conference Proceedings. American Institute of Physics Inc. https://doi.org/10.1063/5.0100387

Ofori, P., 2017. Production of Potassium Hydroxide (KOH) From Plant Biomass: The Case of Cocoa Pod Husks and Plantain Peels. Kwame Nkrumah University of Science and Technology, Kumasi.

Ogunneye, A., Ibikunle, A.A., Sanyaolu, N.O., R, G.M., 2020. Optimized Carboxymethyl Cellulose preparation from Cocoa Pod. J. Chem Soc. Nigeria 45 No.1.

Olufemi, Ademola Stanford, Olufemi, Ademola S., Olayebi, O.O., Makpah, D.E., 2017. A Novel Process for The Production of Potash from Plant Ash: Leaching Technique.

Ordu, J., Ocheme, E., Mgbahuruke, A., 2011. Physicochemical characterization of cellulose and powder extracts of cocoa pod husk as pharmaceutical excipients. Port Harcourt Med. J. 5 https://doi.org/10.4314/phmedj.v5i3.68629.

Orjuela, W.A., Cardona, E.A., Murillo, W., Méndez, J.J., 2019. Aprovechamiento de la Biomasa Lignocelulósica de la Cadena del Cacao. UN Camino a la Bioeconomia Circular, Ibagué.

Ortiz-R, O.O., Gallardo, R.A.V., Rangel, J.M., 2014. Applying life cycle management of colombian cocoa production. Food Sci. Technol. 34, 62–68. https://doi.org/10.1590/S0101-20612014005000006.

Ortiz-Rodríguez, O.O., Villamizar-Gallardo, R.A., Naranjo-Merino, C.A., García-Caceres, R.G., Castañeda-Galvís, M.T., 2016. Carbon footprint of the colombian cocoa production. Engenharia Agricola 36, 260–270. https://doi.org/10.1590/1809-4430-ENG.AGRIC.V36N2P260-270/2016.

Recanati, F., Marveggio, D., Dotelli, G., 2018. From beans to bar: a life cycle assessment towards sustainable chocolate supply chain. Sci. Total Environ. 613–614, 1013–1023. https://doi.org/10.1016/J.SCITOTENV.2017.09.187.

Sakagami, H., Satoh, K., Fukamachi, H., Ikarashi, T., Shimizu, A., Yano, K., Kanamoto, T., Terakubo, S., Nakashima, H., Hasegawa, H., Nomura, A., Utsumi, K., Yamamoto, M., Maeda, Y., Osawa, K., 2008. Anti-HIV and Vitamin C-synergized Radical Scavenging Activity of Cacao Husk Lignin Fraction, vol. 22. In Vivo (Brooklyn).

Sandesh, K., Shishir, R.K., Vaman Rao, C., 2020. Optimization and comparison of induction heating and LPG assisted acid pretreatment of cocoa pod for ABE fermentation. Fuel 262. https://doi.org/10.1016/J.FUEL.2019.116499.

Serra Bonvehí, J., Ventura Coll, F., 1999. Protein quality assessment in cocoa husk. Food Res. Int. 32 https://doi.org/10.1016/S0963-9969(99)00088-5.

Syamsiro, M., Saptoadi, H., Tambunan, B.H., 2011. Experimental investigation on combustion of bio-pellets from Indonesian Cacao Pod Husk. Asian J. Appl. Sci. 4, 712–719.

Tejada, C.N., Almanza, D., Villabona, A., Colpas, F., Granados, C., 2017. Characterization of activated carbon synthesized at low temperature from cocoa shell (*Theobroma cacao*) for adsorbing amoxicillin. Ingeniería Y Competitividad 19.

Tessenderlo Chemie NV, 2001. Potassium Hydroxide. In: SIDS Initial Assessment Report for SIAM 13 (Bern).

Tiegam, R.F.T., Tchuifon Tchuifon, D.R., Santagata, R., Kouteu Nanssou, P.A., Anagho, S. G., Ionel, I., Ulgiati, S., 2021. Production of activated carbon from cocoa pods: investigating benefits and environmental impacts through analytical chemistry techniques and life cycle assessment. J. Clean. Prod. 288 https://doi.org/10.1016/J.JCLEPRO.2020.125464.

Titiloye, J.O., Abu Bakar, M.S., Odetoye, T.E., 2013. Thermochemical characterisation of agricultural wastes from West Africa. Ind. Crop. Prod. 47, 199–203. https://doi.org/10.1016/J.INDCROP.2013.03.011.

Torres, M.A., 2019. Obtención de celulosa a partir de la cáscara de cacao ecuatoriano (*Theobroma cacao* l.) mediante hidrólisis térmica para la elaboración de pulpa de papel. Universidad Central del Ecuador, Quito.

Tsai, C.H., Tsai, W.T., Liu, S.C., Lin, Y.Q., 2018. Thermochemical characterization of biochar from cocoa pod husk prepared at low pyrolysis temperature. Biomass Convers. Biorefin. 8 https://doi.org/10.1007/s13399-017-0259-5.

Tsai, W.T., Bai, Y.C., Lin, Y.Q., Lai, Y.C., Tsai, C.H., 2020. Porous and adsorption properties of activated carbon prepared from cocoa pod husk by chemical activation. Biomass Convers. Biorefin. 10 https://doi.org/10.1007/s13399-019-00403-7.

UGRA, U. de G. de R.A, 2020. Ficha de inteligencia: Cacao. [WWW Document]. URL https://www.finagro.com.co/sites/default/files/ficha_de_inteligencia_-_cacao.pdf (accessed 9.18.23).

Vásquez, Z.S., de Carvalho Neto, D.P., Pereira, G.V.M., Vandenberghe, L.P.S., de Oliveira, P.Z., Tiburcio, P.B., Rogez, H.L.G., Góes Neto, A., Soccol, C.R., 2019. Biotechnological approaches for cocoa waste management: a review. Waste Manag. 90, 72–83. https://doi.org/10.1016/J.WASMAN.2019.04.030.

Villamizar, Y.L., Rodriguez, J.S., León, L.C., 2017. Caracterización fisicoquímica, microbiológica y funcional de harina de cáscara de cacao (*Theobroma cacao* L.) variedad CCN-51. Cuad. Act. 9, 65–75.

Vriesmann, L.C., de Mello Castanho Amboni, R.D., De Oliveira Petkowicz, C.L., 2011. Cacao pod husks (*Theobroma cacao* L.): composition and hot-water-soluble pectins. Ind. Crop. Prod. 34, 1173–1181. https://doi.org/10.1016/J.INDCROP.2011.04.004.

Yapo, B.M., Besson, V., Koubala, B.B., Koffi, K.L., 2013. Adding value to cacao pod husks as a potential antioxidant-dietary fiber source. Am. J. Food Nutr. 1, 38–46.