# Life Cycle Assessment of Colombian Cocoa Pod Husk transformation into value-added products

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## Dedication

*To me, for deciding to fulfill this dream that I had put off for years and maintaining the determination to graduate with honors.*

*To my mother Martha, and my brother Camilo, for providing me with their unwavering support, love, and trust in all my decisions and projects.*

*Though my father is no longer with me, he taught me the importance of education, effort, resilience, and kindness that continue to serve as guiding principles in my life.*

*To my director Aída Luz Villa, who provided invaluable support during the most challenging times.*

*To my closest friends, for their unwavering support over so many years and for always being present with so much affection.*

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## List of acronyms

| | |
|---|---|
| AC | Activated carbon |
| AOAC | Association of official analytical collaboration |
| CAH | Cellulose by autohydrolysis |
| CAT | Cellulose by alkaline treatment |
| CF | Carbon Footprint |
| $CF_m$ | Midpoint Characterization Factor |
| CPH | Cocoa Pod Husk |
| DCB | Dichlorobenzene |
| EDX | Energy dispersive X-Ray analysis |
| FETP | Freshwater ecotoxicity potential |
| FEP | Freshwater eutrophication potential |
| FEWn | Food-energy-water nexus |
| FFP | Fossil fuel potential |
| GWP | Global Warming Potential |
| HCl | Hydrochloric acid |
| HTPc | Human toxicity potential |
| ICONTEC | Instituto Colombiano de Normas Técnicas y Certificación |
| ISO | International Organization for Standardization |
| LCA | Life Cycle Assessment |
| LCIA | Life Cycle Impact Assessment |
| MADR | Ministerio de Agricultura y Desarrollo Rural |
| METP | Marine ecotoxicity potential |
| TAP | Terrestrial acidification potential |
| TGA | Thermogravimetric analysis |
| SEM | Scanning Electron Microscope |
| SM | Standard method |
| SOP | Surplus ore potential |
| WCP | Water consumption potential |

## Abstract

The cocoa production is an important activity for the economic development of the agro-industrial sector in Colombia. The production of dry cocoa beans generates agricultural residues that exceed the edible part of the crops. The highest volume of residues from cocoa is derived mainly from the shells known as cocoa pod husk (CPH), representing 65 to 75% of the fruit's wet weight, with a traditional practice of managing them by outdoor degradation on-farm. The physicochemical characterization of CPH reveals its promising potential to obtain value-added products. In this contribution, the Life Cycle Assessment (LCA) was conducted on the use of Colombian CPH to produce activated carbon, potassium hydroxide and cellulose. Activated carbon was obtained through pyrolysis, employing KOH as the activating agent. Potassium hydroxide was obtained via ash leaching from CPH, followed by caustification. Cellulose was obtained using alkaline treatment and autohydrolysis. As a result, the environmental impact is significantly reduced when CPH is considered a co-product, instead of to being disposed of in open fields where it decomposes organically. With respect the product-value obtained, for the four transformation processes assessed, the production of KOH showed the best environmental performance, followed by cellulose obtained through autohydrolysis, cellulose obtained through alkaline treatment, and finally activated carbon. It was found that electricity consumption during the transformation process emerging as the primary contributor in the impact evaluation, and 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, attributed to the release of mineral nutrients that ultimately leach into freshwater bodies. A sensitivity analysis was conducted to evaluate the effects of a different type of energy source. When solar drying is considered for CPH pretreatment instead of drying in an oven at the laboratory, the impact quantification significantly decreases, with cellulose showing the greatest decrease around 63.1%, followed by KOH with 55.8% and finally activated carbon with a reduction of 31.9%. The energy requirement in the transformation processes is the main contributor in the evaluated impact categories. In future projects, it is recommended to focus on the optimization of the transformation processes utilized in this study to reduce the energy requirements and integrate renewable energy sources. The value-added products obtained possess favorable properties, making them suitable for various potential applications, of which the one with the least environmental impact is the production of KOH from CPH.

*Keywords:* Life cycle assessment, cocoa pod husk, biowaste, activated carbon, potassium hydroxide, cellulose.

# 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 smallholders farmers, many of them located in vulnerable and post-confict regions (Abbott et al., 2018). In 2021, there were aproximately 65000 cocoa-producing families in Colombia and the subsector generated 167000 direct and indirect jobs (MADR, 2021); furthermore, Colombia started as a member of the the International Cocoa Organization (ICCO, 2021) which classified the 95% of cocoa produced as fine flavor and aroma. During the last decade, the national cocoa production has increased significantly, from 37202 tons in 2011 to 62158 tons of cocoa beans in 2022. Based on 2022 production data, the departments with the highest participation in the cocoa production are Santander, Arauca, Antioquia, Tolima, Huila and Nariño with 36.8%, 16.9%, 8.3%, 5.8%, 5.7% and 5.4% of the colombian production, respectivily (Fedecacao, 2023).

The *Theobroma cocoa L.* (Cocoa) tree is a specie of the Malvaceae family and botanically the cocoa is considered berry-like fruit. Cocoa is one of the main export commodities for many tropical countries. About 5.58 million tonnes of dry cacao beans were produced worldwide in 2021 on 11.5 million hectares (FAO, 2021) in the geographical area between 20 N and 20 S of the Equator. About 70% of world Cocoa production comes from West Africa and the rest is produced in South and Central America (De Souza et al., 2018). Cocoa trees develops well in relatively warm climate, with a maximum average of 30 – 32°C and a minimum average of 18 – 21°C. The cacao tree makes optimal use of available light and the shade is essential in his early years. A relatively high humidity is necessary for the optimum development of the cocoa tree and annual rainfall level between 1500 and 2000 mm is preferred because it is very sensitive to soil water deficiency (The Lindt & Sprüngli Farming Program, 2022).

In general context, there are three varieties of cocoa: Criollo, Forastero and Trinitario. Criollo is native to Central and South America as well as the Caribbean islands. Criollo varieties are highly vulnerable to various environmental threats and have lower yields compared to other varieties. Forastero is primarily cultivated in Africa, Ecuador, and Brazil, and it represents approximately 80% of the world's cacao production. It exhibits much greater resistance and lower susceptibility to diseases compared to Criollo varieties. Trinitario is hybrid variety resulted from a cross between Forastero and Criollo varieties. Trinitario predominates in Colombia and it is characterized by a high level of variability in terms of shape, form, size, and behavior. This subspecies is being used in the selections of the materials that are being cloned and recommended by Fedecacao (Abbott et al., 2018).

The cocoa fruit 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 65-75% in dry weight of the fruit, which implies a wide area for its conventional disposal and a serious challenge in waste management. CPH is generated as residual biomass and can be roughly calculated based on the cocoa production yield, pod index (number of beans per pod), bean index (dry bean weight) and proportion of the CPH weight in relation to the total pod weight; for example, in 2022, approximately 559422 tons of CPH were generated. The transformation of CPH into goods represents a great potential to mitigate the impact associated with this biowaste and for implementing a circular economy in the cocoa production industry, thereby maximizing economic development along the cocoa production chain.

Previously, various evaluations have been conducted regarding the utilization of CPH to obtain 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 & Ventura Coll, 1999), food fibers (Yapo et al., 2013), lignocellulosic components (Adeleye et al., 2022; Akinjokun et al., 2021; Torres, 2019), and pectin (Chan & 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, Adesulu-Dahunsi, et al., 2019; Martínez et al., 2015) and biochemical (Antwi et al., 2019; Sandesh et al., 2020) conversion processes. These studies highlight the significant potential of transforming this biowaste into value-added products that can substitute the need for chemical sources and non-renewable energy, thereby mitigating the environmental, social, and economic impacts of linear economies.

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. 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). It enables the evaluation of the sustainability of a process or product and identifies critical points where optimization and/or substitutions are necessary to minimize environmental impact.

## 1.1. Objectives

The general objective of this research was to determine the environmental performance to produce caustic potash, activated carbon and cellulose from Colombian cocoa pod husk, using LCA methodology. To achieve this objective, the following specific objectives had to be fulfilled:

1. To perform the inventory analysis of processes involved in the generation of CPH and its transformation to produce caustic potash, activated carbon and cellulose.

2. To quantify the environmental impact categories (human toxicity, climate change, terrestrial acidification, freshwater eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, water use, mineral resource scarcity and fossil resource scarcity) using the LCA methodology to produce caustic potash, activated carbon and cellulose from CPH.

3. To identify the hotspots of the environmental assessment for each of the analyzed transformation processes of CPH and propose alternatives for improvement that could be evaluated in future work.

## 1.2. Report outline

This report is structured into six chapters. Chapter 1 includes the introduction to the cocoa production in the national context, the general characteristics of cocoa cultivation, previous studies on the use of CPH, the definition of the LCA methodology, the main and specific objectives, and an outline of the document. Chapter 2 encompasses a literature review of studies concerning to the characteristics of the CPH, its utilization, and its transformation to obtain goods and energy. Additionally, it explores LCA associated with cocoa, the utilization of its residues, and the valorization of various types of agro-industrial waste. Chapter 3 describes the methodology employed in this study, divided into four sections in accordance with the LCA framework: goal and scope definition, life cycle inventory analysis, life cycle impact assessment and interpretation. Chapter 4 presents the results and analysis related to the inventory, encompassing the compilation and quantification of inputs and outputs of each transformation process. The magnitude and significance of the potential environmental impacts obtained in the impact assessment are exposed and these results are interpreted in relation to the defined goal and scope for this study. This chapter allows to identify 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. At the end of this chapter the characterization of the value-added products obtained from CPH is described. Chapter 5 corresponds to the conclusions and recommendations for future works. Lastly, Chapter 6 contains the references.

## 1.3. Research products

- Poster: *Obtención de productos de interés comercial a partir de cáscaras de mazorca de cacao de un cultivo orgánico de Tolima (Colombia),* “Acto Solemne de Entrega de Resultados y Clausura del Programa Bio-Reto XXI 15:50” (Bucaramanga, May 4-5, 2023).

- Poster: *Transformación de la cáscara de cacao en productos de interés comercial,* IC-EXPOI 2022 (Congreso internacional de Ingeniería) (Medellín, October 27 – 29, 2022).

Manuscript that is currently being submitted:

- *Life Cycle Assessment of Colombian Cocoa Pod Husk transformation into value-added products*.

# 2. Literature Review

The intense farming around the word for food production generates a large amounts of agriculture waste derived from crop activities, usually exceeding the edible parts of the crops. Additionally, the agribusiness sector substantially contributes to biowaste production to produce raw materials such as cotton, cellulose pulp, and bioethanol. This biowaste includes primary residues such as stalks, leaves, roots, peels, husks, cobs, shells, and nuts, varying according to the specific crop type. The large amount of agro-industrial wastes represents a hazard to the environment and human health when they are not properly managed. Conventional practices involve open burning in landfills, composting agricultural residues, covering soil and outdoor degradation. Biowaste burning in landfills results in soil moisture loss, negatively affecting the germination to the next crop, also affects soil fauna and produces greenhouse gases ($CO_2$, CO, $CH_4$, $N_2O$, $SO_2$), aerosols, particulate matter, smoke, and volatile organic compounds. When these agricultural wastes are left in open field their accumulation could contain infested plant material, leading to pest and disease dissemination favoring the loss of the harvest and public health problems; furthermore, the outdoor degradation generates greenhouse gases (Meza-Sepúlveda et al., 2021).

Colombia is a rich country in natural resources and the agro-industrial is an important economic activity for the country (DANE, 2023). The rise in food production and the growing demand for raw materials are anticipated to lead to a substantial increase in agro-industrial waste. The valorization of biowaste to produce bio-products and bioenergy emerges as a key circular economy strategy for more efficient management of these agro-industrial wastes and delivering multiple environmental, social, and economic benefits. Among these benefits are: a) Agro-industrial waste serves as a cost-effective, renewable, and abundant source of raw materials, without compromising food security; b) contributes to minimizing on-farm burning and outdoor degradation, thereby reducing negative impacts on environmental and human health; c) as raw material, it is attractive to both large-scale industries and small-scale processing in rural areas; d) offers the possibility to generate new income in economies at different scales, improving the socio-economic conditions of the involved stakeholders; e) provides an opportunity to implement circular models to balance the demand and supply of food, goods, and energy; f) facilitates the development and evaluation of technologies that can contribute to sustainable development (Meza-Sepúlveda et al., 2021).

In Colombia, there are approximately 188,000 hectares dedicated to cocoa cultivation (MADR, 2021). During the harvest and breaking of cocoa pods through on-farm processing, approximately 80% of cocoa fruit is discarded as residual biomass. This predominantly consists of cocoa pod husks (65-75%), alongside cocoa bean shells and cocoa sweating, which signifies a substantial opportunity to obtain valuable goods and energy by these cocoa residues transformation (Vásquez et al., 2019), yielding environmental, social, and economic benefits.

## 2.1. Cocoa Pod Husk (CPH)

Previous characterizations of CPH show its high potential feedstock to obtain bioproducts and bioenergy. The physicochemical characterization of CPH carried out by several authors is summarized in **Table 1.**

**Table 1**
Reports of physicochemical characterization of CPH

| Parameter | Minimum | Maximum | References |
|---|---|---|---|
| Moisture, % | 6.67 | 16.1 | (Forero-Nuñez et al., 2015; Nguyen & Nguyen, 2017; Orjuela et al., 2019; Syamsiro et al., 2011; Tiegam et al., 2021; Titiloye et al., 2013; Villamizar et al., 2017) |
| Volatile material, % | 49.9 | 74.1 | (Forero-Nuñez et al., 2015; Maleka, 2016; Orjuela et al., 2019; Syamsiro et al., 2011; Tiegam et al., 2021; Titiloye et al., 2013) |
| Ash, % | 6.7 | 13.5 | (Forero-Nuñez et al., 2015; Nguyen & 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, % | 10.43 | 20.5 | (Forero-Nuñez et al., 2015; Orjuela et al., 2019; Syamsiro et al., 2011; Titiloye et al., 2013) |
| Hemicellulose, % | 9 | 37 | (Daud et al., 2014; Vásquez et al., 2019) |
| Cellulose, % | 15.1 | 35.4 | (Daud et al., 2014; Grillo et al., 2019; Vásquez et al., 2019) |
| Lignin, % | 14.7 | 21.4 | (Daud et al., 2014; Vriesmann et al., 2011) |
| Pectin, % | 3.71 | 9.2 | (Chan & Choo, 2013; Daniyan et al., 2014; Maleka, 2016; Vásquez et al., 2019) |
| K mg/100 g | 2716 | 3220 | (Antwi et al., 2019; Vásquez et al., 2019; Vriesmann et al., 2011) |

There is a significant number of studies on the use of CPH establishing several alternatives to give added value to this agricultural biowaste (see **Table 2**). The alternatives include the use of CPH to produce bioenergy through thermochemical processes such as combustion, gasification, pyrolysis and hydrothermal carbonization; to produce biogas by anaerobic digestion; as a catalyst support due to its potassium oxide content for the trans-esterification in the production of biodiesel from vegetable oils; as a binder material for pellets; for the production of biochar and activated carbon by its amount of fixed carbon; for the production of potassium hydroxide and carbonate due to its high potassium content; as source for the extraction of antioxidants like vitamin C and theobromine; the extraction of protein, alimentary fiber, lignocellulosic components and pectin, among others.

**Table 2**

Alternatives of use of CPH for giving it value added

| Use of CPH | References |
|---|---|
| Production of bioenergy through thermochemical conversion | (Adjin-Tetteh et al., 2018; Dahunsi, Adesulu-Dahunsi, et al., 2019; González-Vázquez et al., 2018; Kilama et al., 2019; Martínez et al., 2015) |
| Production of bioenergy through biochemical conversion | (Antwi et al., 2019; Dahunsi, Osueke, et al., 2019; Sandesh et al., 2020) |
| CPH as base catalyst for trans-esterification process | (Ofori-Boateng & Lee, 2013; Sinaga et al., 2018) |
| Production of pellets | (Forero-Nuñez et al., 2015; Ofori et al., 2020; Syamsiro et al., 2011) |
| Production of biochar | (Marín Armijos et al., 2018; Najafabadi et al., 2021; C. H. Tsai et al., 2018) |
| Production of activated carbon | (Cruz, 2012; Eletta et al., 2020; Spessato et al., 2019; Tejada et al., 2017; Tiegam et al., 2021; W. T. Tsai et al., 2020) |
| Production of potassium hydroxides and carbonates | (Afrane, 1992; Daniyan et al., 2014; Kone et al., 2020; Maliki et al., 2020; Odunlami et al., 2020; Ofori, 2017) |
| Extraction of antioxidants | (Campos-Vega et al., 2018; Nguyen & Nguyen, 2017; Sakagami et al., 2008; Yapo et al., 2013) |
| Extraction of protein | (Serra Bonvehí & Ventura Coll, 1999) |
| Extraction of alimentary fiber | (Yapo et al., 2013) |
| Extraction of lignocellulosic components | (Adeleye et al., 2022; Akinjokun et al., 2021; Daud et al., 2013, 2014; Gatot S. Hutomo, 2012; Ogunneye et al., 2020; Torres, 2019) |
| Extraction of pectin | (Chan & Choo, 2013; Franco Castillo et al., 2010; Muñoz-Almagro et al., 2019; Syamsiro et al., 2011; Vriesmann et al., 2011, 2012) |

Regarding the value-added products of interest in this study for the use of the CPH, the following is highlighted:

Caustic potash is a raw material used in many applications, to produce potassium and agricultural chemicals, soaps, detergents, drain cleaners, paint 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). Currently, the industrial method to produce KOH on a large scale is by electrolysis of potassium chloride solutions (Tessenderlo Chemie NV, 2001). Other unconventional methods have been investigated to obtain KOH through the leaching of ashes obtained from organic matter rich in potassium such as CPH, coconut husk and plantain peel (See **Table 2**). For this process, the CPH undergoes calcination at temperatures ranging from 550 to 700 °C to extract primarily potassium carbonate from the resulting ashes. The extracted carbonate is subsequently leached and causticized to obtain potassium hydroxide. The yield achieved in this process is 0.3%, with a purity of 80.7% (Ofori, 2017).

Activated carbon is very important for the chemical industry in the production of catalysts, adsorbents for heavy metals and organic pollutants, from liquid or gas phase, to storage gas and desalinate media. The most common method to obtain commercial activated carbon is from fossil coals and wood and its cost is relatively high. The production of activated carbon from biomass has been widely studied because it is cheap, renewable and it is a widely available source generated mainly from agro-industrial activities (Blachnio et al., 2020). To obtain activated carbon from CPH biomass, the raw material undergoes a pre-treatment process that involves drying and fine grinding; then, the material is subjected to chemical activation using inorganic salt such as KOH, $ZnCl_2$, or $K_2CO_3$. Carbonization is then carried out at different temperatures and times to obtain the desired properties of BET surface area, pore volume, average pore size and bulk density (Cruz, 2012; Eletta et al., 2020; W. T. Tsai et al., 2020).

Cellulose is the most abundant natural polymer (polysaccharide) on Earth. It can be obtained from wood, forestry wastes, agricultural crops, other vegetables fibers, some bacteria, and algae. Due to its versatile chemical structure, cellulose can be physically and chemically modified in different types and 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). To extract cellulose from CPH biomass, the material is subject to an alkaline treatment with NaOH solution and thermal treatment to obtain unbleached hydrated cellulose pulp. This pulp can then be processed through a bleaching process or dried directly to obtain the product (Akinjokun et al., 2021; Dos Santos et al., 2015; Gatot S. Hutomo, 2012). Another employed method is the autohydrolysis, which involves the treatment of the CPH biomass to high temperature in a steam explosion cell. This process does not require any reagent and results in higher yields, although the purity percentage is lower compared to the alkaline process (Torres, 2019).

There is important progress in the research of technologies to add-value to waste from cocoa production. However, it is essential to conduct a quantitative evaluation of the potential environmental impacts that can be generated from their implementation. To achieve this, the Life Cycle Assessment (LCA) methodology can be employed to determine the environmental performance through the evaluation of various impact categories of different systems along the cocoa production chain and the utilization of its biowastes.

## 2.2. Life Cycle Assessment

The Life Cycle Assessment (LCA) methodology considers the guidelines of the standard ISO 14040 and it is a useful tool to assess the environmental performance of products and processes. LCA 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 is useful for (ICONTEC, 2007):

- To identify hotspots to improve the environmental performance of products throughout the stages of their life cycle.
- To provide information for decision making in the industry, governmental and non-governmental organizations (for example, the strategic planning, designs and redesign of products and processes).
- To design environmental performance indicators and measurement techniques.
- Marketing elements (for example, implementation of labels with an environmental declaration of the product).

LCA deals with environmental aspects and potential environmental impacts throughout the life cycle of a product, process, or technology, within the system boundary. The LCA methodology comprising four phases (see **Figure 1**), usually carried out iteratively to allow for adjustments based on new insights, as outlined below:

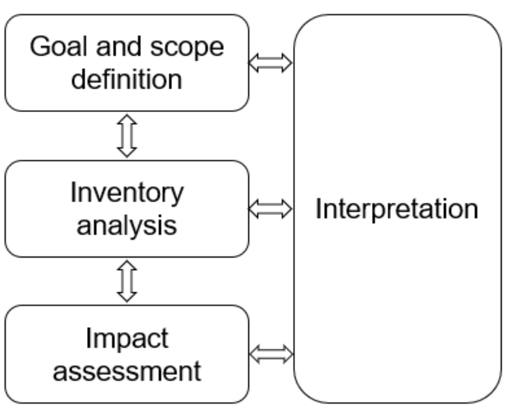



**Figure 1.** Phases of LCA methodology

1. *Goal and scope definition:* The goal and scope must be clearly defined and consistent with the application of the process to be treated. This step elucidates the study's objective and indicates the intended use of the results or application. The following points should be taken into consideration in accordance with ISO 14044 standard (ISO, 2006):

- The product system to be studied - establishing the framework for conducting the LCA.
- The functions of the product system, or systems for comparative studies.
- The "functional unit" - serves as a measure of the function of the studied system, and it provides a reference point to which the inputs and outputs can be correlated. This enables the comparison of two or more fundamentally distinct systems.
- The system boundary - determines which unit processes are included or excluded in the LCA. These are determined considering factors such as the intended application of the analysis, underlying assumptions, exclusions, the type and quality of available data, limitations, and other relevant considerations.

The system boundary is defined through detailed characterization of the product system, and it should be consistent with the goal and scope. The approach can be gate-to-gate, cradle-to-gate, cradle-to-grave, or cradle-to-cradle. Gate-to-gate considers only the design and production process in whole production chain; cradle-to-gate considers from material extraction (cradle) to the factory gate (production process); cradle-to-grave is the complete LCA from material extraction through production process, distribution, use and final disposal stage including related transport in whole production chain; cradle-to-cradle considers the complete LCA and admits the recovery or/and recycling of the outputs of the waste disposal of the system (Chancharoonpong, 2020b). The system boundaries for LCA are illustrated in **Figure 2.**

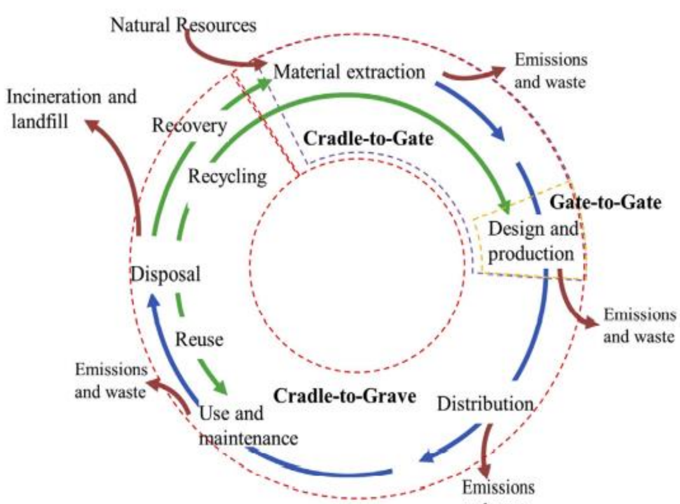



**Figure 2.** System boundaries for LCA methodology (Shah et al., 2016)

- Allocation procedures – which attribute shares of the total environmental impact to the various products within a system. Inputs and outputs must be allocated to different products in accordance with clearly defined procedures, which should be documented and explained alongside the allocation procedure.

Allocation procedures should closely align with the relationships and characteristics, such as mass balance or economic value, that are established for inventory inputs and outputs (See **Table 3** and **Table 4**) (Chancharoonpong, 2020a). Outputs may consist of products, co-products, and waste in varying proportions. It is necessary to identify the ratio between these components, as the impacts will be allocated proportionally to products and co-products.

**Table 3**

Mass allocation procedure

| Product and or co-product | Quantity | % of allocation |
|---|---|---|
| X | a | a / (a+b+c) ×100% |
| Y | b | b / (a+b+c) ×100% |
| Z | c | c / (a+b+c) ×100% |

**Table 4**

Economic allocation procedure

| Product and or co-product | Quantity | Price | % of allocation |
|---|---|---|---|
| X | a | A | aA / (aA+bB+cC) ×100% |
| Y | b | B | bB / (aA+bB+cC) ×100% |
| Z | c | C | cC / (aA+bB+cC) ×100% |

- Impact categories selected and methodology of impact assessment, and subsequent interpretation to be used.

- Data requirements: reliability of the results of LCA study depends on the extent to which data quality requirements are met which includes adequate temporal and geographic coverage, precision, completeness, representativeness, consistency, and reproducibility.

- Assumptions, which encompass engineering estimates or decisions based on values, should be clearly explained considering the analysis conducted on the data.

- Limitations, arising from incompleteness due to cut-offs and a lack of process specificity, need to be identified.

2. *Life cycle inventory analysis (LCI):* All environmentally relevant material and energy flows within the defined product system are quantified and expressed per functional unit. This phase identifies the inventory flows and quantifies them, based on multiple data sources. The relevant steps of the LCI phase include flow diagrams, data collection, data estimation and allocation, ultimately generating the balance sheet of inputs and outputs for each unit process of the study.

According to ISO 14044 (2006), both qualitative and quantitative data employed in the inventory should be collected for each unit process within the system boundary. This data is utilized to quantify the inputs and outputs of a unit process, regardless of whether it is measured, estimated, or calculated. Life cycle inventory (LCI) data is derived from both primary and secondary sources. Primary data is collected through direct measurements within the system boundary, while secondary data originates from other sources such as literature (Chancharoonpong, 2020a).

3. *Life cycle impact assessment (LCIA):* LCIA aims to evaluate the magnitude and significance of the potential environmental impacts associated with impact categories and category indicators. The LCIA phase includes the collection of indicator results for the different impact categories, which together represent the LCIA profile for the product system.

The LCIA phase shall include the following mandatory elements: (1) Selection of impact categories and category indicators; (2) to assign the LCI results to different impact categories (classification); (3) calculation of category indicator results (characterization). Additionally, there are optional steps for LCIA, such as relating the impact indicators to reference conditions (normalization), grouping, and weighting impacts (ISO, 2006).

Impact categories can be expressed as midpoint or endpoint indicators. Midpoint indicators reflect links in the cause-effect chain from activities causing environmental stressors to environmental effects, while endpoint indicators quantify the actual end effects. For example, Global Warming Potential (GWP) serves as a midpoint indicator for climate change, as it is based on the influence of emissions on radiative forcing. On the other hand, endpoint indicators for climate change assess the contribution of emissions to potential consequences of altered radiative forcing, such as sea-level rise, increased frequency of extreme weather events, or the human health implications of rising temperatures (Goedkoop & Spriensma, 2001). Endpoint indicators are categorized into areas of protection, including human health, ecosystem, and resource availability as illustrated in **Figure 3**.

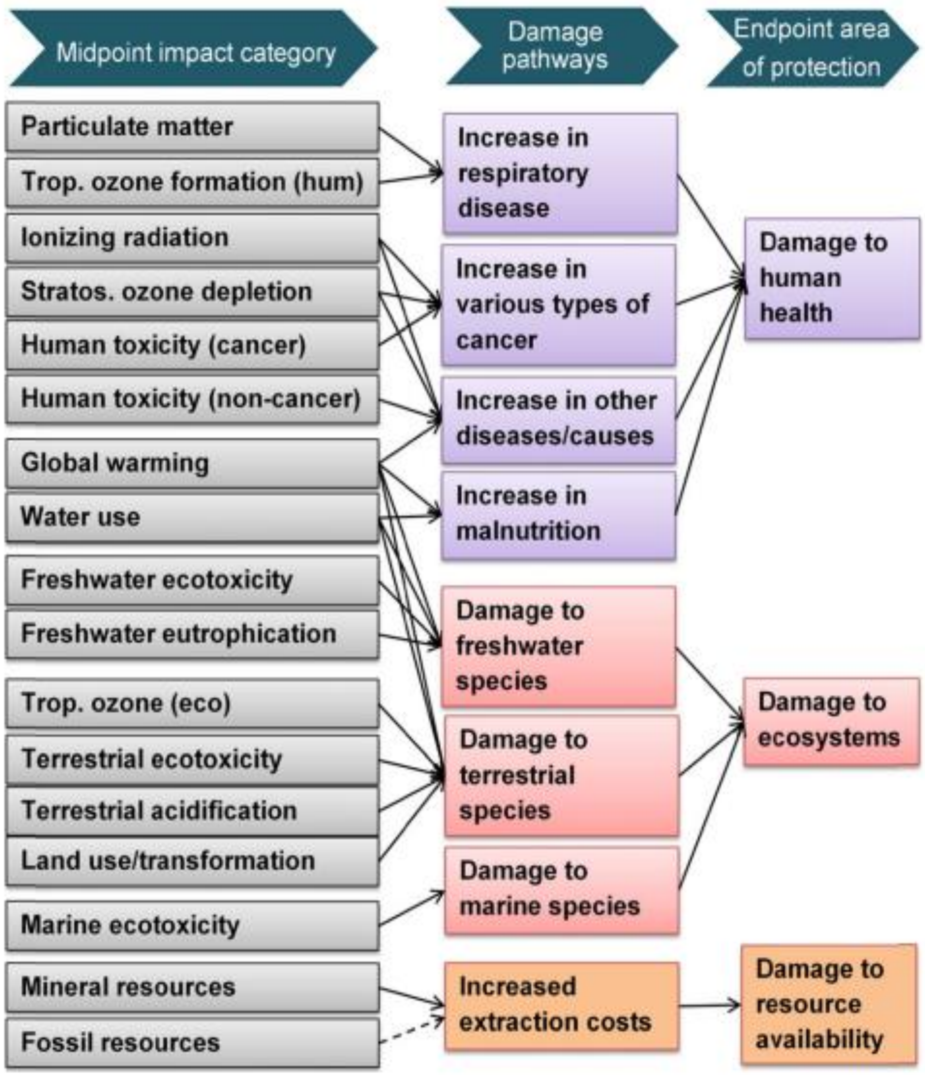



**Figure 3.** Relation between impact categories, indicators, and areas of protection in ReCiPe 2016. *The dotted line means there is no constant mid-to-endpoint factor for fossil resources* (Huijbregts et al., 2017).

The environmental life cycle impact characterization of a substance in an impact category is the change in its intrinsic property responsible for the category due to change in its abundance in the environment relative to the alteration of a reference substance, as described in Equation 1:

$$LCIA_{i=x,k} = \frac{\int_0^{TH} a_{i=x,k}x(t)dt}{\int_0^{TH} a_{i=r,k}r(t)dt} \quad (1)$$

$LCIA_{i=x,k}$ is the life cycle impact characterization of a substance $x$ in an impact category $k$. $a_i$ is the intrinsic property of the substance $x$ or relative substance $r$ for its unit concentration change in the environment. The function of time $(t)dt$ is the change in abundance due to instantaneous release or depletion of the substance. $TH$ is the time horizon of the computation. The unit of life cycle impact characterization of a substance correspond to the ration with respect to a reference substance, and it is expressed as the mass of the reference substance equivalent (Sadhukhan et al., 2021).

Optional elements of LCIA, such as normalization, involve calculating the magnitude of category indicator results relative to reference information. Normalization can provide understanding of the importance of impacts compared to a reference. Grouping encompasses sorting and potentially ranking the impact categories. Weighting involves converting and possibly aggregating indicator results across impact categories using numerical factors based on value-choices (ISO, 2006).

Various software options are available for performing the calculations of the LCIA phase using inventory data. **Table 5** lists the most used commercial software (Becerra, 2021).

**Table 5**
Software to perform LCIA phase (Becerra, 2021)

| Software | Developer | Main applications of LCA |
|---|---|---|
| SimaPro | PRé-Consultants | Industry, consulting, research, and academy; efficient value chains; eco-friendly design; eco-efficiency; carbon footprint; potential environmental impact with statistical precision; environmental product declarations. |
| Gabi | Pe-International | Ecological design; efficient value chains; eco-efficiency. |
| Umberto | Ifu Hamburg GmbH | Industry, consulting, research, and academy; integrated cost accounting; hotspots identification; energy efficiency and resource optimization. |
| OpenLCA | GreenDelta GmbH | Industry, consulting, research, and academy. |
| eBalance | IKE Environmental Technology, China | Industry, consulting, research, and academy. |
| eime | Bureau Veritas CODDE, France | Industry, consulting, research, and education; eco-design routes; environmental policies. |
| Quantis Suite | Quantis Intl, Switzerland | Eco-design of products; environmental policies; Carbon footprint. |

Databases are used as data packages in the software to perform the LCIA phase. Database consists of a set of related data that can be modified according to the disposition and extent of information. The most frequently used includes (Becerra, 2021):

- Ecoinvent: The largest and employed in applications across various industries.
- Agri-footprint: Utilized for agriculture, food, and biomass.
- Agribalyse: Applied in the fields of agriculture and food.
- Datasmart LCI: Used for textiles, packaging, biomaterials, and milk products.
- ELCD: Specifically employed for chemistry and metallurgy.

- Environmental Footprint Database: Suitable for general industries.
- Exiobase: Applied in environmental, economic, and social applications.
- WEEE LCI: Focused on electricity and electronics.

Different impact assessment methods have been developed by various organizations to perform the LCIA. Some of these are Eco-indicator 99 (Goedkoop & Spriensma, 2001); IPCC 2013 GWP100a (Dentener et al., 2013) and ReCiPe 2016 (Huijbregts et al., 2017). ReCiPe 2016, employed in this study, provides characterization factors representative on a global scale across 18 groups of impact categories. It encompasses both midpoint (problem-oriented) and endpoint (damage-oriented) impact categories, available for three different perspectives: individualistic (I), hierarchical (H), and egalitarian (E). These perspectives do not claim to represent archetypes of human behavior; rather, they are employed to group similar types of assumptions and choices. For example (Pre' Consultants, 2016):

- The Individualist perspective (I) is based on the short-term interest, impact types that are undisputed, and technological optimism regarding human adaptation.
- The Hierarchist perspective (H) is based on the most commonly accepted policy principles concerning timeframes and other issues.
- The Egalitarian perspective (E) is the most precautionary, considering the longest timeframes and all impact pathways for which data is available.

4. *Interpretation:* It is defined by NTC-ISO 14040 as the 'phase of LCA in which the finding of either the inventory analysis or the impact assessment, or both, are evaluated in relation to the defined goal and scope to reach conclusions and recommendations' (ICONTEC, 2007). Life Cycle Interpretation is a systematic technique to identify, quantify, verify, and evaluate information derived from the results of the life cycle inventory and/ or the life cycle impact assessment. The interpretation phase has two primary objectives: firstly, to analyze results, reach conclusions, explain limitations, and provide recommendations; secondly, to present the results of an LCA study in a readily understandable, comprehensive, and consistent manner, aligning with the goal and scope of the study (Chancharoonpong, 2020a).

The LCA methodology was applied to the primary process of cocoa production in Colombia, where the stages of nursery sowing, site preparation, planting and vegetative growth were analyzed (Ortiz-R et al., 2014). This study used data from 30 farms from Santander, North of Santander, and Antioquia. Ortiz et al. (2014) 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 highest emission was 607 kg$CO_2$-eq (per ha per year), where the use of synthetic fertilizers in high doses was the largest contributor to this environmental impact. Cropping practices and supply consumption are different between farms; negative GWP values were observed for farms where improved practices such as organic fertilization was used, which implies a contribution to reducing environmental impacts in terms of $CO_2$ emissions (Ortiz-R et al., 2014).

The carbon footprint (CF) of the Colombian cocoa production was evaluated by Ortiz-Rodriguez et al. (2016) comparing agricultural practices under two scenarios: conventional and agroforestry managements. For the production scenarios, post-harvest activities were considered, and the data were obtained from farms in the departments of Santander, Antioquia, Arauca, Huila, and North of Santander. With the conventional management yields are low (between 400 to 500 kg of cocoa/ha), old tools are used to prevent susceptibility to pest and diseases instead of using herbicides and fungicides; and no chemical or foliar fertilizers are used. Otherwise, the agroforestry reaches yield between 1200 and 1500 kg of cocoa/ha, and it features using clones CCN-51, ICS-39 and hybrid, that have high resistance to pests and diseases. 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 more than 85% of emissions over the CF (Ortiz-Rodríguez et al., 2016).

Along with the LCA other important indicators have been analyzed, such as the food-energy-water nexus (FEWn), which was included in the study carried out in Bolivia country for four types of cocoa production: agroforestry under conventional management (CA), agroforestry under organic management (OA), full-sun monoculture under conventional management (CM), and full-sun monoculture under organic management (OM). The results show that conventional compared with organic management, has all larger negative environmental impacts. For instance, the GWP of conventional production management was approximately 2.5 times higher than in their organic counterparts. Fertilizers and crop protection were the major contributors of conventional systems for the impact categories: abiotic depletion, terrestrial ecotoxicity, acidification and eutrophication. Further, it was found that CA systems had better environmental performance than OM due to the diversification of the production. Integrated analysis with FEWn proved that agroforestry systems, and particularly OA, are more energy-efficient and more efficient in the use of water than monocultures, highlighting that OA management produces more food/energy per unit of water used (Armengot et al., 2021).

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. As process outputs are mainly dried beans and CPH in a ratio of 1:4.5 (Leyte et al., 2017), there is a clear opportunity to produce value-added products from CPH. Tagne et al. (2020) 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. (2017) 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 accumulation of CPH due to its open field disposal could contain infested plant material, leading to pest and disease dissemination favoring the loss of the harvest and public health problems (Devi et al., 2017). As mentioned by Ortiz-Rodríguez et al. (2016), the anaerobic decomposition of CPH left on the ground generates methane and nitrous oxide; the negative impact on climate change due to the generation of CPH during the harvest was also identified by Leyte et al. (2017). Other indicators such as abiotic depletion also have a negative impact when CPH is not considered as a co-product according to the sensitivity analysis carried out by Recanati et al. (2018).

A similar study applying the LCA methodology to evaluate the use of agro-industrial waste to obtain value-added products was carried out by Ortiz-Sanchez et al. (2021). This study assessed the global environmental impact of various scenarios related to orange peel waste (OPW) production, disposition, and valorization using a life cycle assessment approach. Four scenarios were examined: (i) Orange juice production with OPW landfilling; (ii) Orange juice production and OPW valorization under the low complexity biorefinery context, comprised the extraction of essential oil by steam distillation, biogas and fertilizer production by anaerobic digestion; (iii) Orange juice production and OPW valorization under the medium complexity biorefinery context, included the extraction of essential oil and pectin by hydrolysis, and the resulting solid was used for the production of biogas and fertilizer; and (iv) Orange juice production and OPW valorization under the high complexity biorefinery context, comprised the extraction of essential oil, hesperidin by supercritical fluid extraction, pectin, biogas, and fertilizer, as well as the production of acetone, butanol, and ethanol by fermentation. The environmental assessment results revealed that the agronomic stage had the highest contribution in the total orange processing chain. Conversely, the scenario with the highest environmental impact was associated with OPW disposal in landfills. The utilization of OPW to obtain added-value products demonstrated more environmentally friendly through the concept of biorefinery. OPW valorization contributes to reducing greenhouse gases emissions, water releases, and fossil fuel use. Low complexity biorefineries exhibited the lowest environmental impact, attributed to their low energy demand and waste flows. In contrast, more complex processes require higher energy and mass inputs. The environmental impact was directly proportional to the biorefinery complexity (Ortiz Sanchez et al., 2021).

Life cycle assessment has been sparingly applied in case studies exploring the utilization of agro-industrial waste to obtain value-added products. From the reviewed references, it is evident that LCA has not been employed to assess the transformation of Colombian cocoa pod husk into value-added products such as caustic potash, activated carbon, and cellulose. This research project is designed to address this gap and fulfill the aforementioned purpose.

# 3. Methodology

The research methodology for this project was developed within the framework of the four phases of the LCA under guideline of ISO standards 14040 and 14044.

## 3.1. Goal and scope definition

The aim of this study was to assess the environmental performance of utilizing CPH to produce caustic potash, activated carbon and cellulose. This work adopts a cradle-to-gate approach, whose boundaries are identified in section 3.1.2., including the agricultural phase of cocoa cultivation to their on-farm processing where the CPH is generated, up to production of caustic potash, activated carbon and cellulose. The data of production of organic cocoa system was obtained from ten agroforestry farms of the association *Héroes del cultivo* in the rural zone of San Bernardo-Ibagué (Colombia).

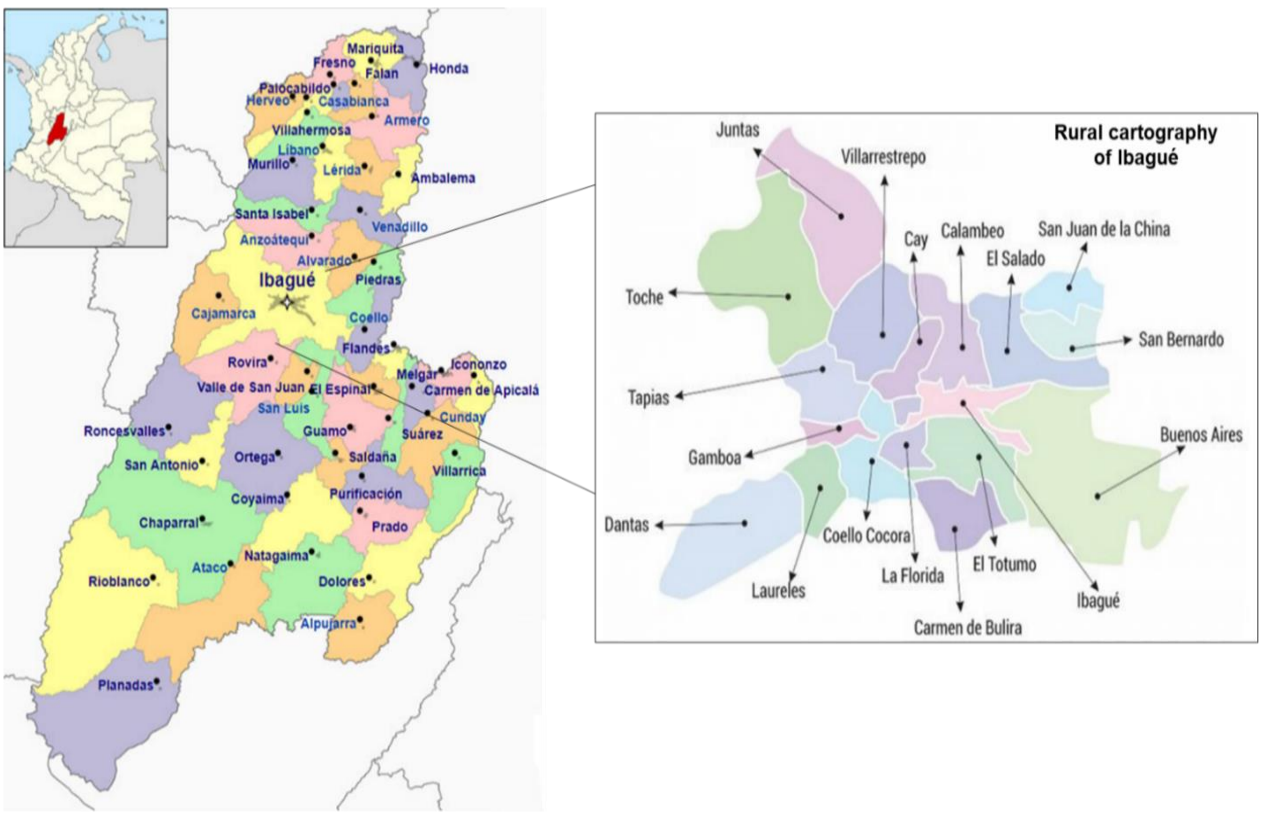



**Figure 4.** Geographic location of studied cocoa crops (adapted image[1])

[1] (Ibague online, 2022) (Centro de información municipal para la planeación participativa, 2022)

The agroforestry farms grow three varieties of cocoa: mainly the Criollo, followed by the Trinitario and in a smaller proportion the Forastero. The cocoa *(Theobroma cacao L.)* is cultivated in associations with other plants and/or tress to provide shade. Farmers mainly introduce lemon and tangerine that are planted between cocoa trees as well timber tree and other shading trees (Robinson Tapiero, personal interview, 24th October 2022). The cultivation of cocoa-agroforestry aims at diversifying products and minimizing the use of agrochemicals.

### 3.1.1. Functional unit

For this study, 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.

### 3.1.2. System boundaries

This study adopts a “cradle to gate” approach, encompassing the extraction of the main raw material (CPH) until to obtain the value-added products. To assess this, it was necessary to evaluate organic cocoa production and quantify the impacts associated with generating Cocoa Pod Husk (CPH), which were then incorporated into the inventory of the subsequent transformation processes to produce value-added products. 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. Detailed explanations for each system are provided in the following subsections: 2.1.2.1. Organic cocoa production, 2.1.2.2. Activated carbon production from CPH, 2.1.2.3. Potassium hydroxide production from CPH, and 2.1.2.4. Cellulose production from CPH.

#### *3.1.2.1. Organic cocoa production*

The cocoa production process includes the stages of stablishing the crop starting with the nursery, site preparation, planting, and vegetative growth, where Supermagro, lime, water and gasoil are required; the harvest stage where the CPH is generated, and the processing in the benefit plant corresponding to fermentation where the mucilage undergoes incomplete oxidation, solar drying and packing to obtain dry cocoa bean packed in jute bag to market as a final product. The complete description of each stage for the organic cocoa production, the inputs and outputs per stage are described in the section 3.2.1. Organic cocoa production. The stages of organic cocoa production process and the system boundary are illustrated in **Figure 5.**

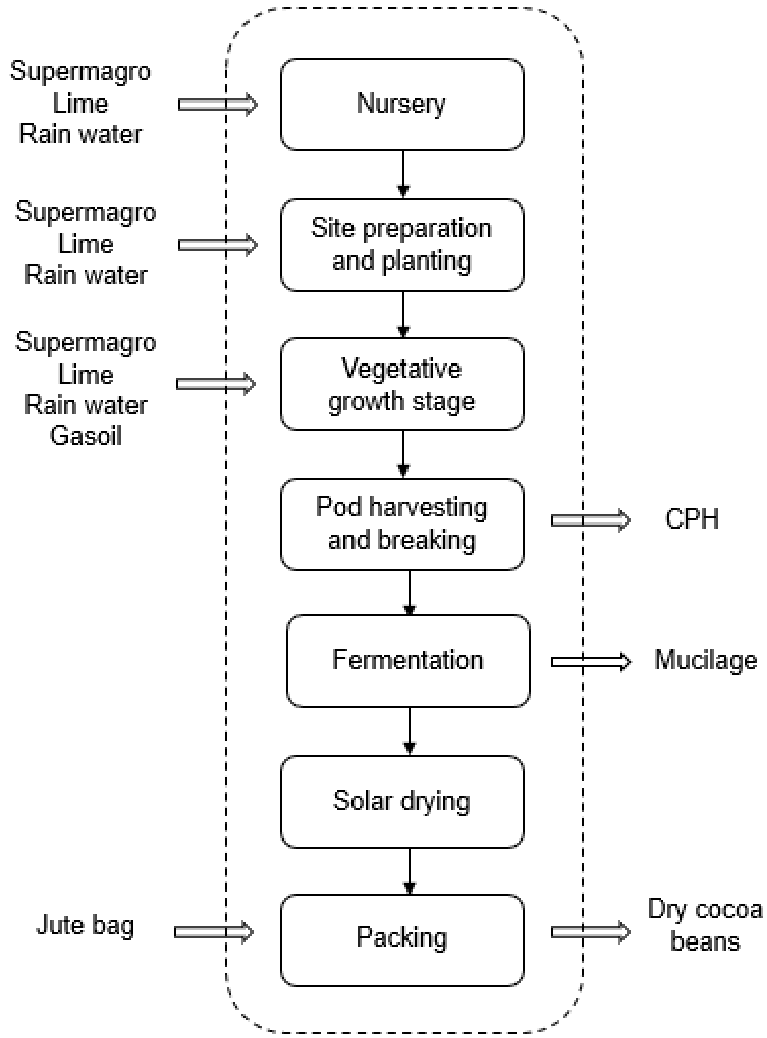



**Figure 5.** System boundaries for organic cocoa production (Author)

#### *3.1.2.2. Activated carbon production from CPH*

The system boundaries to produce activated carbon include the stages from the CPH pretreatment corresponding to drying and grinding, where CPH is considered a co-product of organic cocoa production process, and it has associated the impact assessment of its generation. Other stages of transformation process correspond to chemical activation with KOH, drying, pyrolysis under a nitrogen atmosphere, neutralization with HCl, washing and a final drying to obtain the activated carbon as shown in **Figure 6.** The experimental methodology, equipment, the inputs, and outputs per stage are described in section 3.2.2. Activated carbon production from CPH.

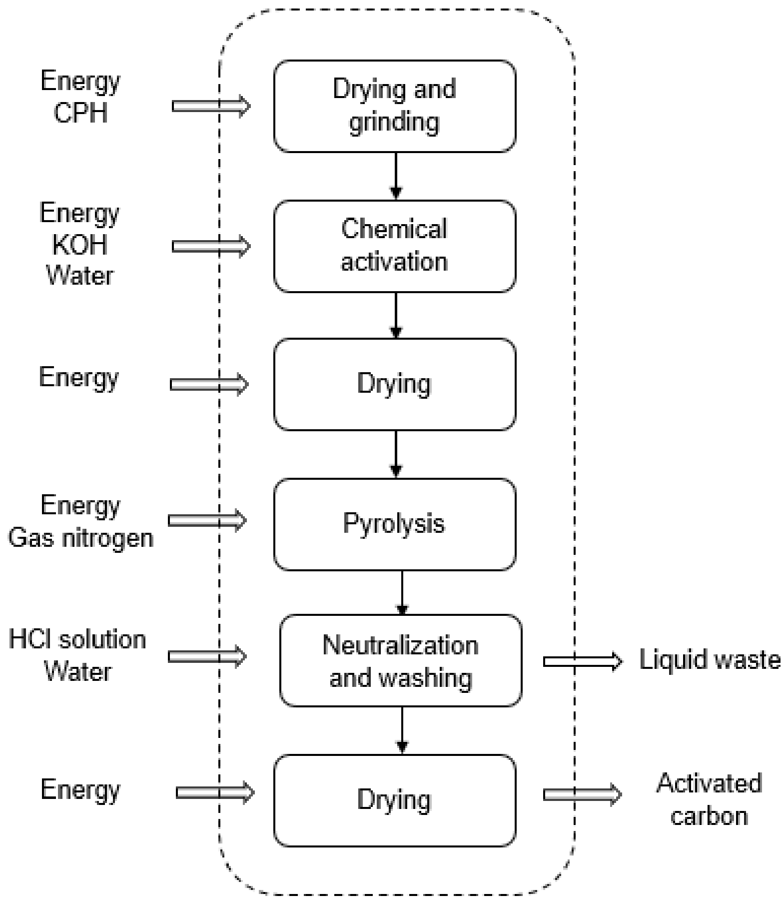



**Figure 6.** System boundaries for activated carbon production (Author)

#### *3.1.2.3. Potassium hydroxide production from CPH*

The system boundaries for this process include the stages from the CPH pretreatment corresponding to drying and grinding, where CPH is considered a co-product of organic cocoa production process, and it has associated the impact assessment of its generation. Other stages of transformation process are shown in **Figure 7**. This correspond to calcination to obtain the ashes that are leached, filtration and evaporation to obtain a mixture with a higher proportion of $K_2CO_3$ and a lower proportion of KOH, then a caustification is performed using calcium hydroxide in an aqueous medium to precipitate calcium carbonate and extract potassium hydroxide in solution. Filtration is then conducted to separate the precipitate, followed by evaporation to obtain KOH. The experimental methodology, equipment, the inputs, and outputs per stage are described in section 3.2.3. Potassium hydroxide production from CPH.

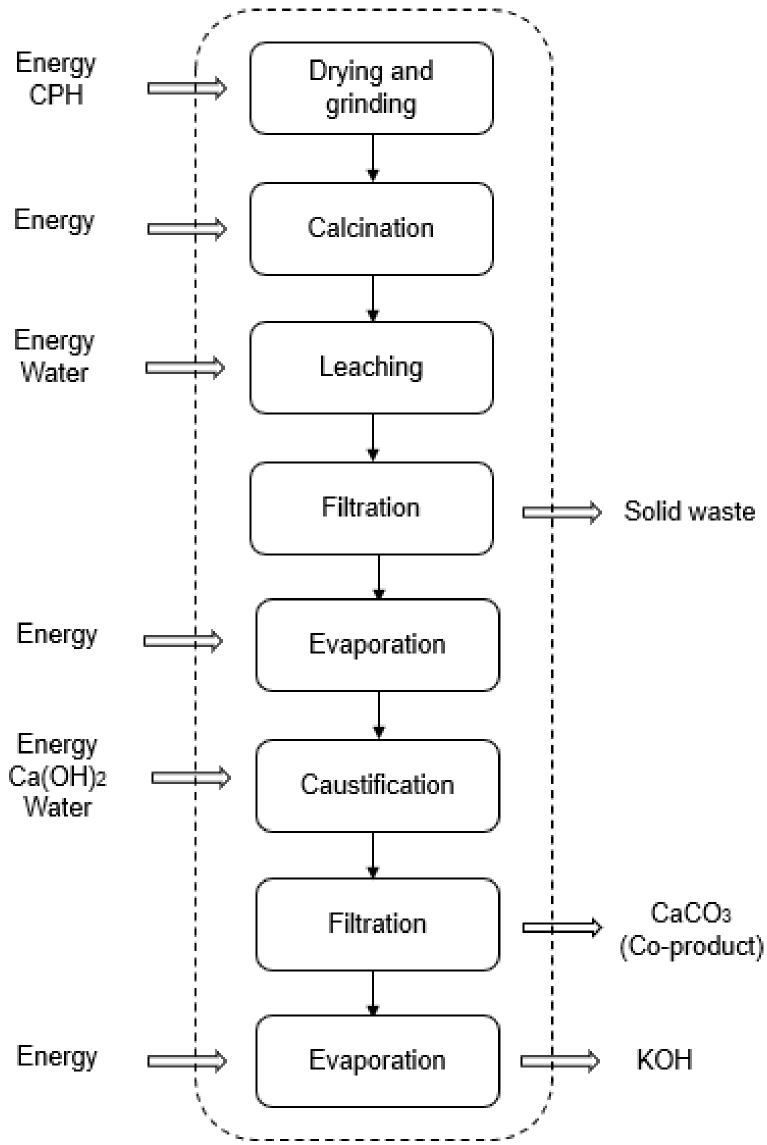



**Figure 7.** System boundaries for KOH production (Author)

#### *3.1.2.4. Cellulose production from CPH*

Two methodologies were employed to obtain cellulose. One involved the use of an alkaline treatment, while in the other autohydrolysis is used. In both cases, the system boundaries include the stages from the CPH pretreatment corresponding to drying and grinding where CPH is considered a co-product of organic cocoa production process, and it has associated the impact assessment of its generation. The procedures used, equipment, the inputs and outputs per stage are described in section 3.2.4. Cellulose production from CPH. The system boundaries for each one is illustrated in **Figure 8** and **Figure 9. Figure 8** shows the system boundaries for cellulose production by alkali treatment (CAT) with NaOH. Following the alkali treatment, filtration, washing, and drying steps are performed to obtain the cellulose. **Figure 9** illustrates the system boundaries for the cellulose production process via auto-hydrolysis (CAH), which is subsequently followed by filtration and drying stages to obtain cellulose.

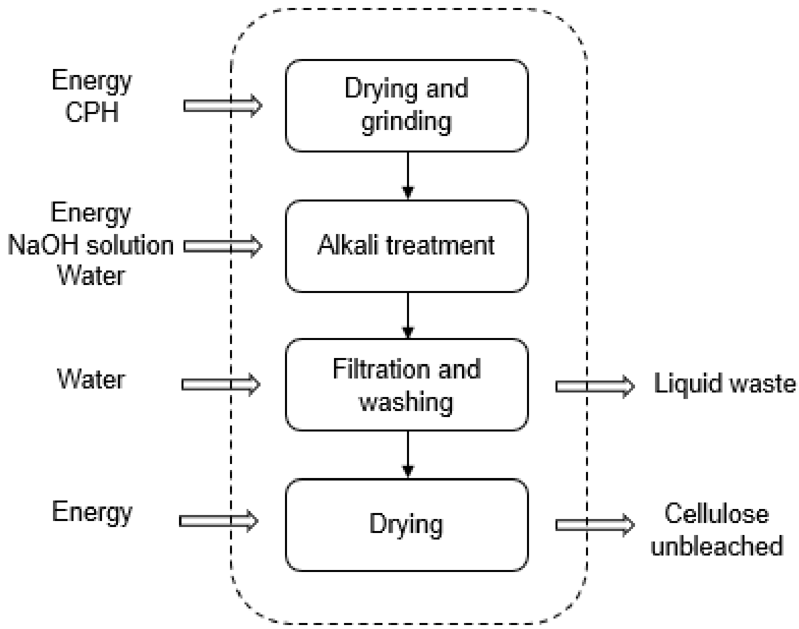



**Figure 8.** System boundaries for cellulose production by alkali treatment (CAT) (Author)

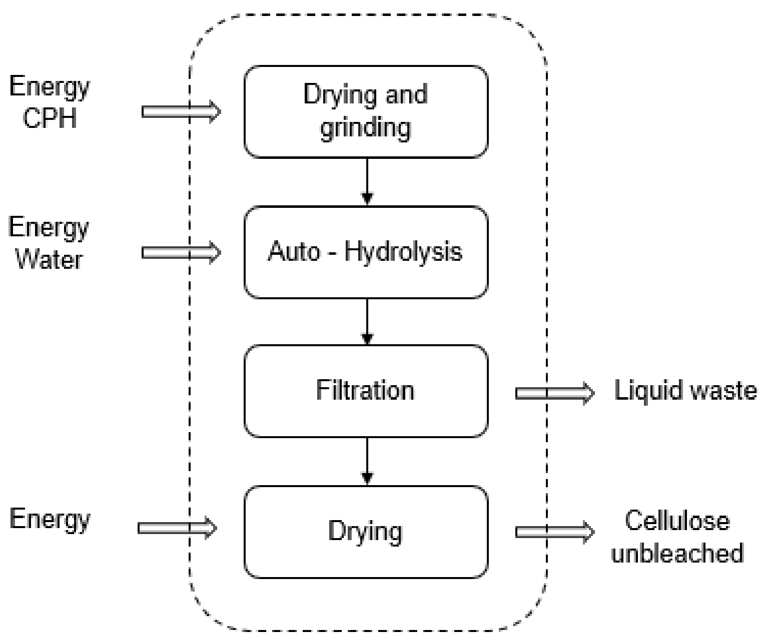



**Figure 9.** System boundaries for cellulose production by auto-hydrolysis (CAH) (Author)

### 3.1.3. Allocation procedures

In this study the allocation was conducted on a mass basis. For the system to evaluate the environmental impact of CPH disposal in open field in the organic cocoa production, only dried cocoa beans remain as the high value product through the analysis for which it has 100% of allocation for impact assignment (See **Figure 10**), and CPH is considered a biowaste that goes out into the technosphere. For transformation processes, CPH is considered as a valuable co-product in the organic cocoa production, which is used as a raw material to produce caustic potash, activated carbon and cellulose. The partition allocation considered for CPH as a co-product in the organic cocoa production is established according to the relation of CPH:Dry cocoa beans (See **Figure 11**).

Documentación | **Entrada/salida** | Parámetros | Descripción del sistema

Productos

| Salidas conocidas a la tecnósfera. Productos y co-productos | Cantidad | Ud. | Cantidad | Asignación % |
|---|---|---|---|---|
| _ORG.COCOA DRIED BEANS HDC \| Cut-Off | 117 | kg | Mass | 100 % |

**Figure 10.** Mass allocation applied in SimaPro to assess CPH disposal in open field

Documentación | **Entrada/salida** | Parámetros | Descripción del sistema

Productos

| Salidas conocidas a la tecnósfera. Productos y co-productos | Cantidad | Ud. | Cantidad | Asignación % |
|---|---|---|---|---|
| _CPH_COPRODUCT \| Cut-off | 1214 | kg | Mass | 88 % |
| _ORG.COCOA DRIED BEANS \| Cut-off | 117 | kg | Mass | 12 % |

**Figure 11.** Mass allocation applied in SimaPro to assess CPH considered a co-product

To assess the transformation process to obtain activated carbon and cellulose, only the respective products were considered as high-value, and 100% mass allocation was applied (See **Figure 12**).

Documentación | **Entrada/salida** | Parámetros | Descripción del sistema

Productos

| Salidas conocidas a la tecnósfera. Productos y co-productos | Cantidad | Ud. | Cantidad | Asignación % |
|---|---|---|---|---|
| _ACTIVATED CARBON FROM CPH \| Cut-Off | 1.55 | g | Mass | 100 % |

**a)**

Documentación | **Entrada/salida** | Parámetros | Descripción del sistema

Productos

| Salidas conocidas a la tecnósfera. Productos y co-productos | Cantidad | Ud. | Cantidad | Asignación % |
|---|---|---|---|---|
| _CELLULOSE UNBLEACHED (CAT) FROM CPH \| Cut-off | 3.2 | g | Mass | 100 % |

**b)**

Documentación | **Entrada/salida** | Parámetros | Descripción del sistema

Productos

| Salidas conocidas a la tecnósfera. Productos y co-productos | Cantidad | Ud. | Cantidad | Asignación % |
|---|---|---|---|---|
| _CELLULOSE UNBLEACHED (CAH) FROM CPH \| Cut-off | 6.2 | g | Mass | 100 % |

**c)**

**Figure 12.** Mass allocation applied in SimaPro to assess the production of: a) activated carbon, b) CAT, and c) CAH

To produce potassium hydroxide, calcium carbonate is obtained as a co-product. Whereby, the impact allocation percentage is distributed between the two products, as it is shown in **Figure 13**.

Documentación | **Entrada/salida** | Parámetros | Descripción del sistema

Productos

| Salidas conocidas a la tecnósfera. Productos y co-productos | Cantidad | Ud. | Cantidad | Asignación % |
|---|---|---|---|---|
| _KOH FROM CPH \| Cut-Off | 1.3 | g | Mass | 52 % |
| _Calcium Carbonate | 1.2 | g | Mass | 48 % |

**Figure 13.** Mass allocation applied in SimaPro to assess the production of potassium hydroxide from CPH

### 3.1.4. Data requirements

Data sources include primary data collected from field survey of cocoa farmers carried out between April to October 2022 in the rural zone of San Bernardo-Ibagué (**Appendix A**). Additional, secondary data obtained from Eco-invent 3.8 and Agri-footprint 6 database were gathered for support this research. For transformation of CPH into activated carbon, potassium hydroxide and cellulose, laboratory tests were carried out to obtain primary data for mass and energy balances and waste generation. The data of the inventory analysis are reported in section 3.2. Life cycle inventory analysis.

### 3.1.5. Impact assessment categories and method

The impact categories, defined by the ReCipe 2016 (Huijbregts et al., 2017), are: climate change, human toxicity, terrestrial acidification, freshwater eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, water use, mineral resource scarcity and fossil resource scarcity. The midpoint impact category and the characterization factors ($CF_m$) evaluated are listed in **Table 6**.

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. The hierarchical (H) perspective with midpoint ponderation is chosen by default, mainly because the values selected by this version are widely accepted in scientific and political contexts (ecoRaee, 2013).

**Table 6**
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 |

Attributional analysis was applied, which considers the immediate physical input and output flows for the process that are environmentally relevant and provides information about the impacts of these processes without considering the indirect effects of the system, resulting in comparatively lower uncertainty (Shah et al., 2016).

### 3.1.6. Assumptions and limitations

- For the analysis of the organic cocoa production, the first four years from cultivation were considered as the establishment phase of the cocoa crop to start producing cocoa pod.

- The environmental benefits derived from ecosystem services provided by cocoa plantations during the crop phase are not considered due to the complexity associated with acquiring the necessary information to stablish the inventory analysis.

- For the life cycle inventory analysis, irrigation for the cocoa production was not included because the precipitation of the geographic location of the study is sufficient for the development of the crop. The total annual precipitation in the studied area fluctuates between 1725 mm and 2150 mm. For the period from

January to June 2022, the average monthly precipitation was 167 mm, and the average temperature was between 24 °C and 28 °C (IDEAM, 2021).

- For the LCIA, the transformation processes of CPH are assumed to take place in rural zone of San Bernardo-Ibagué, no transportation was considered.

## 3.2. Life cycle inventory analysis

The inventory data consists of associated inputs such as raw materials, resources, and energy; and outputs such as products, co-products, and wastes. Based on the defined system boundary, the life cycle inventory analysis of each system is related in sections 3.2.1 to 3.2.4, corresponding to the organic cocoa production, production of activated carbon, potassium hydroxide and cellulose from CPH.

### 3.2.1. Organic cocoa production

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 an own formulation of the Supermagro biofertilizer and lime. Supermagro is applied once during the first year, twice from the second year and during the mature period until the tree finishes its production in a period between 20 and 25 years of life. Lime is applied two to four times per year. Pest, weed, shadow and shape control is done mechanically with chainsaw, and manually with hacksaw and pruner. The control of pest, weed and shadow in the crop area is carried out from the transplant of the tree; and shape control from the second year (Robinson Tapiero, personal interview, 24th October 2022).

Yield of cocoa pod may fluctuate given certain conditions, such as the age of the tree, disease and pest outbreak and long run of drought mainly. The cocoa yield pattern was estimated based on field data collected within the first half of the year 2022 considering only the first quality cocoa fruit (product). The fruit that does not meet the characteristics of first quality cocoa is classified, a part is completely discarded and the other is used for artisanal products, for consumption on the farm or it is sold at a low price as regular cocoa.

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. CPH is left on the ground and most of the time it is used to prepare compost. 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% (**Figure 14**). Finally, the selected grains are packed in 50-kilogram jute bags and sealed with seams (Robinson Tapiero, personal interview, 24th October 2022). Most of this work in the benefit plant is manual.

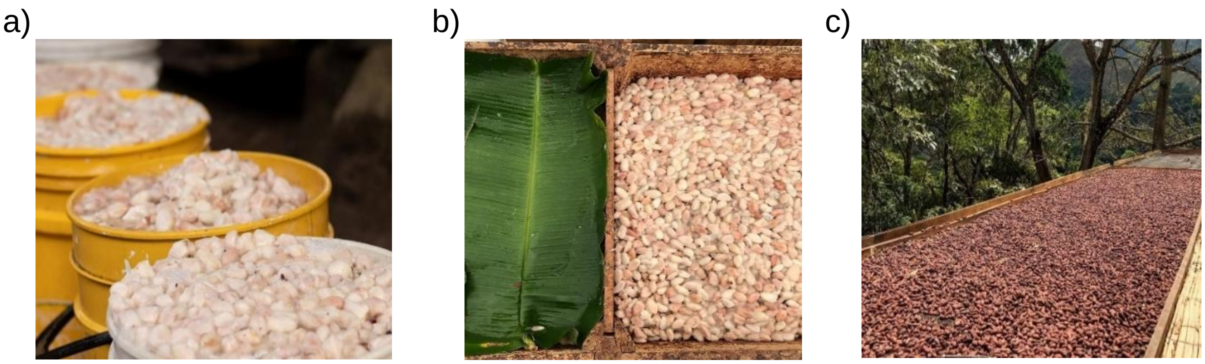



**Figure 14*.*** Post-harvesting at the La Marinilla benefic plant: a) Cocoa in slime in plastic buckets, b) Fermentation, c) Sun drying (juanchoconat, 2021: online[2])

The entire infrastructure of the benefit plant has served the process since 2016. The useful life of the processing plant infrastructure is estimated at 10 years (Robinson Tapiero, personal interview, 24th October 2022); therefore, the plant infrastructure is excluded from the inventory analysis.

To characterize CPH, samples of the Criollo and Trinitario varieties were taken from the La Cascada and Palobayo farms. The pods were processed in the laboratory of *Environmental Catalysis* research group of the Universidad de Antioquia to determine the weight of the fruit, the CPH, the cocoa beans and the mucilage (See **Figure 15**). The physicochemical characterization included determining the humidity (ISO 18134-3:2015), volatile matter (ISO 18123:2015), ashes (ISO 18122:2015), fixed carbon (By subtracting), hemicellulose (Van Soest AOAC 2002.4), cellulose (Van Soest AOAC 973.18), lignin (Van Soest H2SO4), and potassium content (SM 3111B). Additionally, SEM-EDX analysis was conducted. The quantification was done with a 50-50 mixture of the two varieties. The transformation processes were performed using the same mixture of varieties.

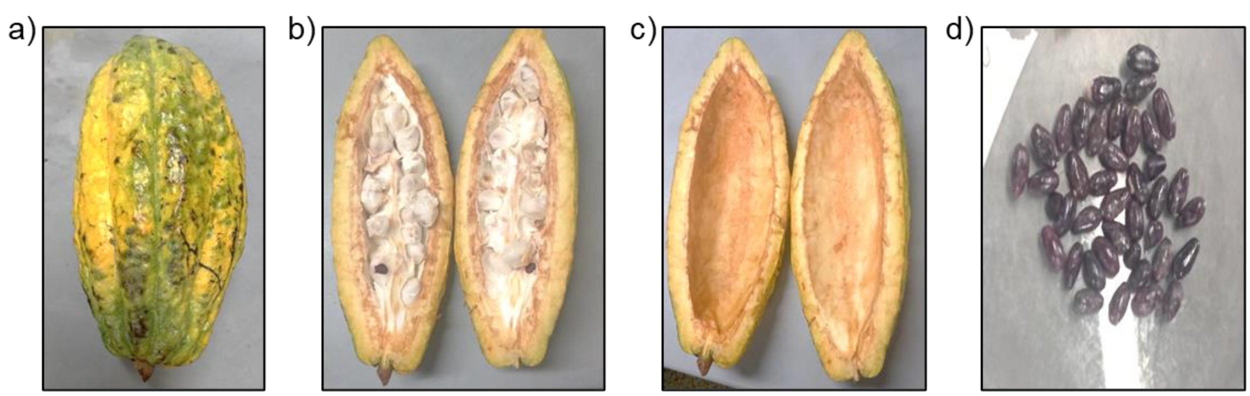



**Figure 15.** Trinitario cocoa fruit processing stages: a) Whole pod, b) Breaking of cocoa pod, c) CPH, d) Cocoa beans (Author)

[2] juanchoconat. (2021) [Online] [Accessed 29th April 2023] https://instagram.com/juanchoconat?igshid=YmMyMTA2M2Y=

The impacts associated with the CPH due to its generation during the organic cocoa production process were quantified and charged to the inventory of the transformation processes to obtain potassium hydroxide, activated carbon and cellulose.

The type and source of data used to establish the inventory analysis are detailed in **Table 7**.

**Table 7**

Type and source of data used for the organic cocoa production

| Life cycle inventory data | Data source | | Reference |
|---|---|---|---|
| | **Primary data** | **Secondary data** | |
| The amount of raw material from the technosphere. | X | | Robinson Tapiero, personal interview, 24th October 2022 |
| Data for raw materials production. | | X | Ecoinvent database 3.8 and Agri-footprint database 6.0 |
| The number of resources from nature. | | X | (IDEAM, 2021) |
| Data for resources use. | | X | Ecoinvent database 3.8 |
| The amount of product, co-product and biowaste generated. | X | | Robinson Tapiero, personal interview, 24th October 2022 and laboratory analysis. |

### 3.2.2. Activated carbon production from CPH

Activated carbon was produced following the methodology described in **Figure 16**. First, CPH was dried (BINDER APT.line ED260) and ground (AMBER MOE005002-CM157). CPH with a particle size less than 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 mix to water). The impregnation stage was carried out in a beaker using a magnetic stirring plate (Heidolph Instruments MR Hei-Standard) at 500 rpm at room temperature. The impregnated CPH was dried at room temperature for 12 h and then at 80°C for 5.5 h using an oven (Lindeberg Blue M01420A). The dried material placed in a ceramic crucible was pyrolyzed in a furnace (Vulcan 3-130) in nitrogen atmosphere for 3 h at 500° (Cruz, 2012; W. T. Tsai et al., 2020). After the pyrolysis process, the obtained solid was washed with a 1 M HCl aqueous solution (MERCK) and then with distilled water (Tiegam et al., 2021). Finally, the activated carbon was dried at 80°C (Lindeberg Blue M01420A) and sieved. The obtained activated carbon was characterized by SEM-EDX to semiquantitatively determine its composition and analyze its structure. Additionally, an isotherm analysis was conducted using nitrogen as adsorbate in the Sortometer Micrometrics (ASAP 2020 PLUS).

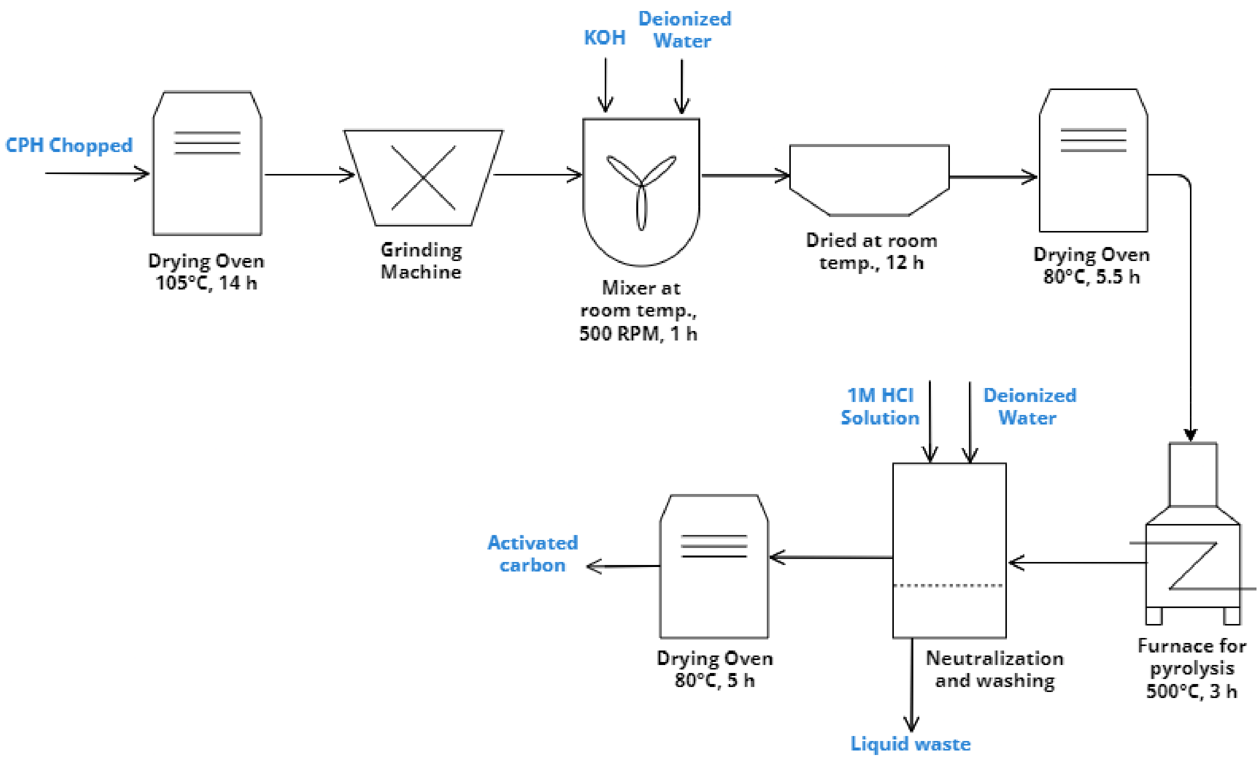



**Figure 16.** Activated carbon production process (Author)

The type and source of data used to establish the inventory analysis are detailed in **Table 8**.

**Table 8**
Type and source of data used for the activated carbon production

| Life cycle inventory data | Data source | | Reference |
|---|---|---|---|
| | Primary data | Secondary data | |
| The amount of raw material from the technosphere. | X | | Laboratory-scale process |
| Data for raw materials production. | | X | Ecoinvent database 3.8 and Agri-footprint database 6.0 |
| The number of resources and energy used during the production process. | X | | Laboratory-scale process and equipment specifications. |
| Data for resources and energy use. | | X | Ecoinvent database 3.8 |
| The amount of product and waste generated. | X | | Laboratory-scale process |

### 3.2.3. Potassium hydroxide production from CPH

The methodology of the process is illustrated in **Figure 17**. The production of potassium hydroxide started with drying (BINDER APT.line ED260) and grinding (AMBER MOE005002-CM157) of CPH. CPH with a particle size lower than 90 µm was placed in a ceramic crucible and calcinated at 650°C for 1 h in a furnace (Vulcan 3-130). 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 (Equation 2). At the same time, a small part of potassium carbonate reacted with water vapor to produce potassium hydroxide and bicarbonate (Equation 3) (Olufemi et al., 2017).

$$K_2O\ (s) + CO_2(g) \rightarrow K_2CO_3(s) \quad (2)$$

$$K_2CO_3(s) + H_2O(g) \rightarrow KOH(s) + KHCO_3(s) \quad (3)$$

The ashes obtained that contained mainly $K_2CO_3$, were leached with water at a weight ratio of 1:10 (ash:water). The leaching process was performed in a reflux system using a plate with heating and magnetic stirring (Heidolph Instruments MR Hei-Standard) at 80°C and 500 rpm for 1 h. During the leaching process, the residual $K_2O$ reacted with water to form soluble KOH. 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 on a hot plate (Heidolph Instruments MR Hei-Standard) until the water was completely evaporated to obtain the solid product (Daniyan et al., 2014). By titration, the percentage of $K_2CO_3$ and KOH of the product obtained was determined. Then, a caustification process was carried out using calcium hydroxide (MERCK) to produce KOH and calcium carbonates a precipitate (Equation 4) (Ofori, 2017). The caustification was performed in an aqueous medium, with gradual heating to 80°C on a hot plate with reflux system and magnetic stirring (Heidolph Instruments MR Hei-Standard). The new alkaline solution was allowed to cool, filtered to obtain the extract that was heated at 90°C on a hot plate (Heidolph Instruments MR Hei-Standard) until the water was completely evaporated to obtain the solid material.

$$K_2CO_3(s) + Ca(OH)_2(aq) \rightarrow 2KOH(aq) + CaCO_3(s) \quad (4)$$

The potassium hydroxide content of the obtained material was determined through acid-base titration using the double-indicator method. Initially, the phenolphthalein indicator was added to the aliquot, and 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).

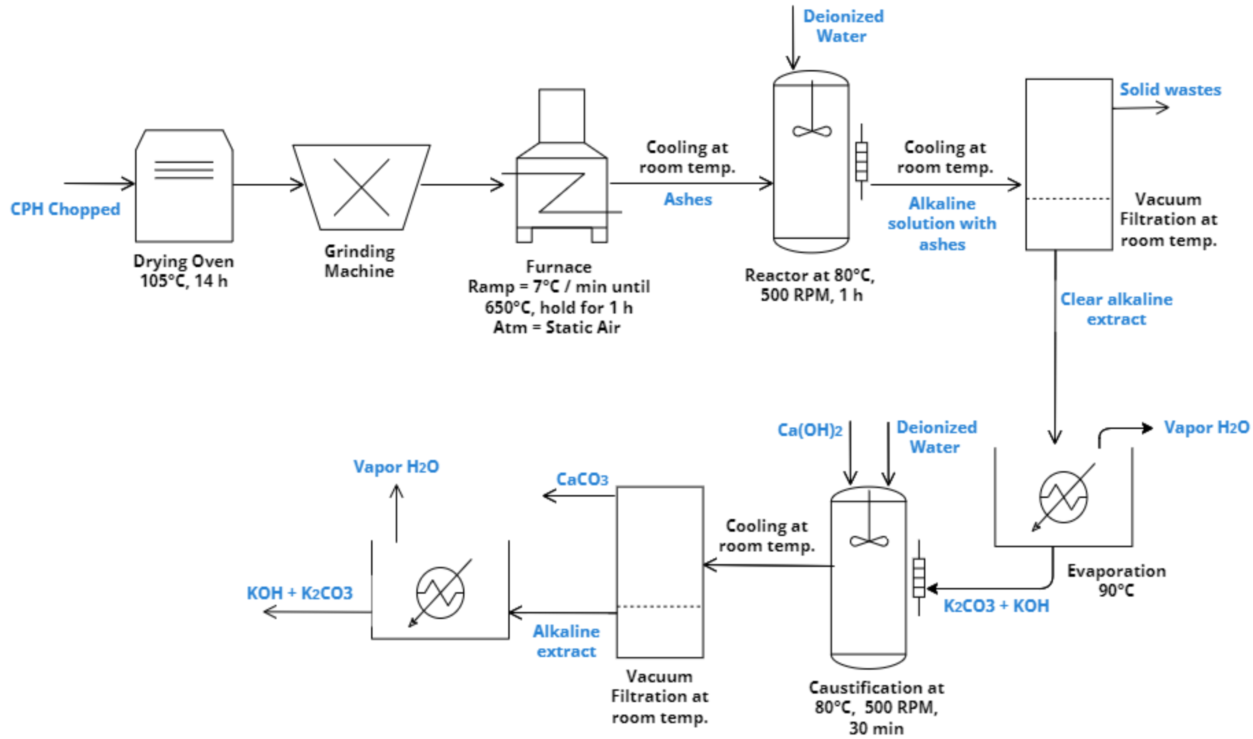



**Figure 17.** Potassium hydroxide production process (Author)

The type and source of data used to establish the inventory analysis are detailed in **Table 9**.

**Table 9**
Type and source of data used for the potassium hydroxide production

| Life cycle inventory data | Data source | | Reference |
|---|---|---|---|
| | Primary data | Secondary data | |
| The amount of raw material from the technosphere. | X | | Laboratory-scale process |
| Data for raw materials production. | | X | Ecoinvent database 3.8 and Agri-footprint database 6.0 |
| The number of resources and energy used during the production process. | X | | Laboratory-scale process and equipment specifications. |
| Data for resources and energy use. | | X | Ecoinvent database 3.8 |
| The amount of product and waste generated. | X | | Laboratory-scale process |

### 3.2.4. Cellulose production from CPH

For both, alkaline treatment and autohydrolysis process to produce cellulose, the CPH was dried (BINDER APT.line ED260) and ground (AMBER MOE005002-CM157) before obtaining particle size less than 90 µm.

The alkaline treatment methodology is described in **Figure 18**. CPH was treated with a 2% NaOH solution (PanReac) in a solid:liquid ratio of 1:20 (CPH:NaOH solution). The alkaline treatment was performed in a reflux system using a plate with heating and magnetic stirring (Heidolph Instruments MR Hei-Standard) at 90°C and 600 rpm for 2 h. The obtained slurry was filtered with a vacuum equipment and the solid material was washed with distilled water until the alkali was removed (Dos Santos et al., 2015). The product obtained was dried in an oven (Lindeberg Blue M01420A) at 80°C for 4 h.

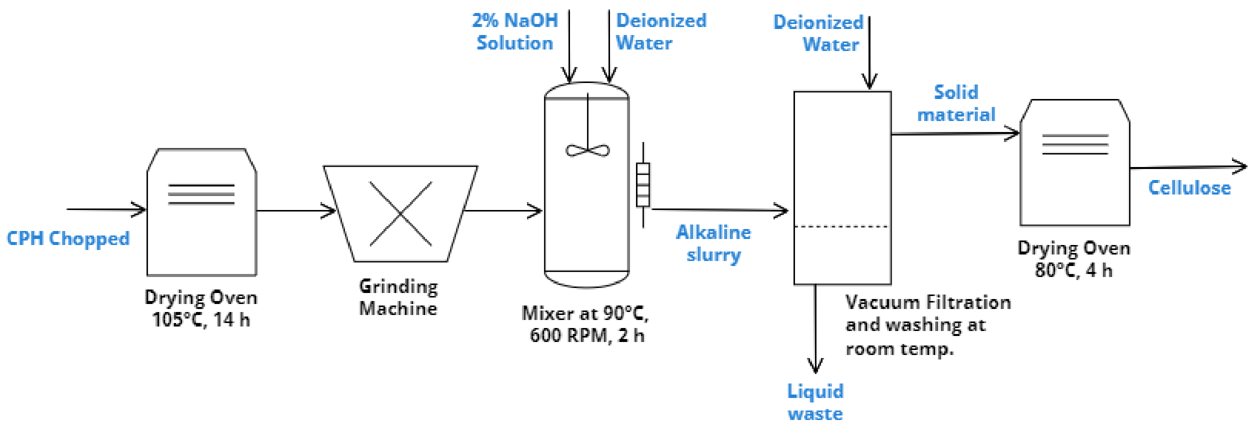



**Figure 18.** Cellulose production process through alkaline treatment (Author)

The autohydrolysis methodology is described in **Figure 19**. 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 minutes. The slurry was then cooled at room temperature and filtered using vacuum equipment to obtain the hydrated solid product that was dried in an oven (Lindeberg Blue M01420A) at 80°C for 4 h (Torres, 2019).

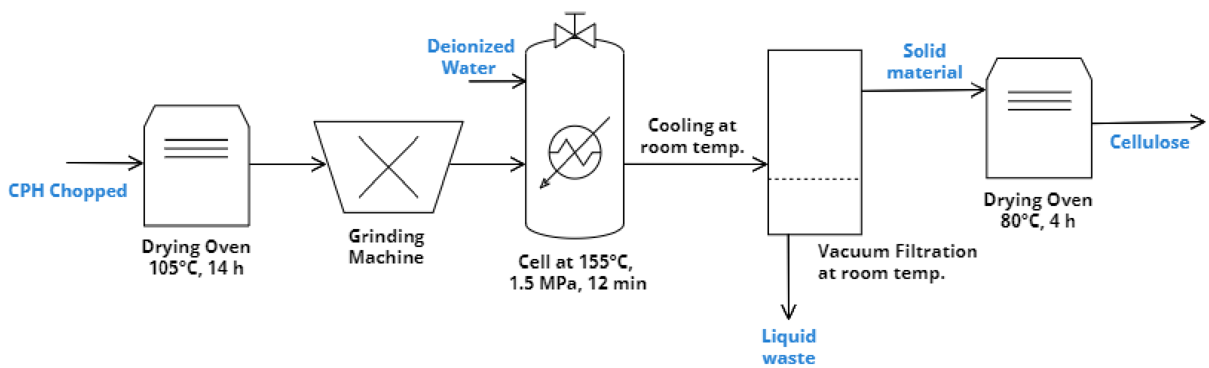



**Figure 19.** Cellulose production process through autohydrolysis (Author)

**Table 10** provides the type and source of data to stablish the inventory used for cellulose production using the two methodologies followed in this research.

**Table 10**
Type and source of data used for cellulose production

| Life cycle inventory data | Data source | | Reference |
|---|---|---|---|
| | Primary data | Secondary data | |
| The amount of raw material from the technosphere. | X | | Laboratory-scale process |
| Data for raw materials production. | | X | Ecoinvent database 3.8 and Agri-footprint database 6.0 |
| The number of resources and energy used during the production process. | X | | Laboratory-scale process and equipment specifications. |
| Data for resources and energy use. | | X | Ecoinvent database 3.8 |
| The amount of product and waste generated. | X | | Laboratory-scale process |

## 3.3. Life Cycle Impact Assessment (LCIA)

To quantify the potential environmental impact of each product, the ReCiPe Midpoint (H) method was used as the life cycle impact assessment. The environmental impacts indicators were chosen according to the widespread use in cocoa industry LCA studies and other previous studies related to the products of interest mentioned in section 2.1. This study included 10 Midpoint indicators listed in ReCiPe2016 as follows (Huijbregts et al., 2017):

*1. Climate change:* the characterization factor used is GWP, expressed in kg $CO_2$-eq, which quantifies the integrated infrared radiative forcing increase of a greenhouse gas.

*2. Human toxicity cancer:* the characterization factor used is HTPc, expressed in kg 1.4-DCB-eq to urban air, which indicates the risk increase of cancer disease incidence because of chemical emissions.

*3. Terrestrial acidification:* the characterization factor used is TAP, expressed in kg $SO_2$-eq to air, which quantifies the proton increase in natural soils by acid deposition. This expresses the potential for acid rain.

*4. Freshwater eutrophication:* the characterization factor used is FEP, expressed in kg P to freshwater-equivalents, which quantifies the phosphorus forms increase in freshwater.

*5. Terrestrial ecotoxicity:* the characterization factor used is TETP, expressed in kg 1.4-DCB-eq to industrial soil, which quantifies the hazard-weighted increase in natural soils due to the chemical emissions.

*6. Freshwater ecotoxicity:* the characterization factor used is FETP, expressed in kg 1.4-DCB-eq to freshwater, which quantifies the hazard-weighted increase in freshwaters due to the chemical emissions.

*7. Marine ecotoxicity:* the characterization factor used is METP, expressed in kg 1.4-DCB-eq to marine water, which quantifies the hazard-weighted increase in marine water due to the chemical emissions.

*8. Water use:* the characterization factor used is $m^3$ of water consumed per $m^3$ of water extracted.

*9. Mineral resource scarcity:* the characterization factor used is SOP, expressed in kg Cu-eq, which expresses the average extra amount of ore produced in the future caused by the extraction of a mineral resource considering all future production of that mineral resource.

*10. Fossil resource scarcity:* the characterization factor used is FFP, expressed in kg oil-eq, which is define as the ratio between the higher heating value of a fossil resource and the energy content of crude oil.

## 3.4. Interpretation

At this phase of LCA, the results of the life cycle inventory and the LCIA are summarized, analyzed, and interpreted for each product. The outcome of this phase corresponds to the conclusions and recommendations of the study carried out. In the interpretation it is intended (1) to assess the environmental performance to produce caustic potash, activated carbon and cellulose from CPH, and (2) to identify the source of the environmental issue for each of the analyzed transformation processes of CPH and propose alternatives for improvement in future work.

# 4. Results and analysis

The life cycle inventory analysis focused on identifying the inputs and outputs associated with resources, materials, energy, products, co-products, and waste generated throughout the organic cocoa production process and the subsequent transformation processes to obtain activated carbon, KOH, and cellulose from CPH. For the organic cocoa production process, the physicochemical properties of CPH samples were obtained through characterization conducted at the laboratory of the Environmental Catalysis research group at the Universidad de Antioquia. Using the inventory analysis results, an impact assessment (LCIA) was conducted for the organic cocoa production process. A comparison was made between the scenario where CPH is considered bio-waste that decomposes in open fields and the scenario where it is treated as a co-product. The findings revealed a significant reduction in impact quantification when CPH is considered a co-product. Then, the comparative LCIA was carried out for the transformation processes to obtaining value-added products from CPH. The evaluation highlighted that KOH exhibited the best environmental performance among the assessed products, with electricity identified as the main contributor to the LCIA for the evaluated transformation processes. Finally, in the characterization of the products obtained from CPH, it became evident that activated carbon, potassium hydroxide, and cellulose have favorable properties, rendering them suitable for various potential applications.

## 4.1. 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 the following four subsections. In the supplementary material, **Appendix B**, it is indicated the specifications of the equipment used, data of raw materials and information used from Ecoinvent database 3.8 and the Agri-footprint database 6.0.

### 4.1.1. Life cycle inventory analysis of organic cocoa production

To establish the inventory of the organic cocoa production process, the cocoa fruit and CPH were characterized. The cocoa fruit are oval and consists of three main parts, the cocoa beans, the mucilage, and the cocoa pod husk as shown in **Figure 20**. The dry cocoa beans represent the only commercially valuable product, and they are used for manufacturing of chocolate and other cocoa products.

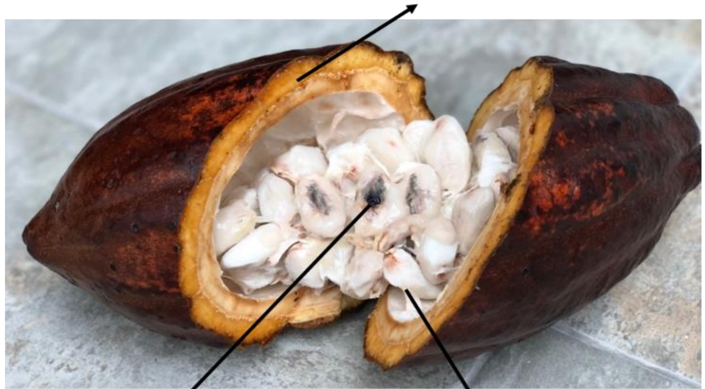



**Figure 20.** The cocoa fruit structure (Author)

The Criollo and Trinitario varieties of cocoa fruit were analyzed in the laboratory of the Environmental Catalysis research group at the Universidad de Antioquia. The weight of CPH and dry cocoa beans corresponded to 73.6% ± 1.3% and 7.4% ± 0.3% of the fruit's weight, respectively. The ratio of CPH generated in relation to the dry cocoa beans produced is approximately 10:1 (CPH:Dry cocoa beans); furthermore, the CPH has a moisture content of 85.5%, which was determined following ISO 18134-3. The results of the analyzed fruits are shown in **Table 11**.

**Table 11**
Physical characteristics of cocoa fruits

| | Criollo variety fruits | | Trinitario variety fruits | | Total average |
|---|---|---|---|---|---|
| | Average* | σ | Average* | σ | |
| Fruit weight (g) | 672.3 | 9.8 | 673.9 | 7.2 | 673.1 |
| CPH weight (g) | 485.9 | 9.1 | 504.6 | 9.4 | 495.3 |
| Dry cocoa beans weight (g) | 49.2 | 3.5 | 49.6 | 3.7 | 49,4 |
| | | | | | |
| CPH with respect the fruit (%) | 72.3 | 2.3 | 74.9 | 0.6 | 73.6 |
| Dry cocoa beans with respect the fruit (%) | 7.1 | 0.4 | 7.7 | 0.2 | 7.4 |
| Relation CPH: Dry cocoa beans | 9.8 | 0.5 | 10.2 | 0.2 | 10 |
| CPH Moisture (%) | 85.5 | 0.7 | 85.4 | 3.2 | 85.5 |

* The average corresponds to three fruits of each of the varieties analyzed.

The thermogravimetric analysis (TGA), conducted in a nitrogen atmosphere on the CPH samples, revealed that the moisture and volatile matter content was 3.6% and 72.9% respectively, on a dry matter basis. Moisture content was determined by measuring the constant weight loss at 107°C, while the volatile matter content was measured as weight loss after exposing the CPH at 900°C for 10 minutes (refer to **Figure 21**). The ashes, determined as the residue after burning to a constant weight at 550°C according to EN ISO 18122, correspond to 8.5%. The content of fixed carbon calculated with Equation 5 was 15%.

$$\%Fixed\ carbon = 100 - (\%Moisture + \%Volatile + \%Ash) \quad (5)$$

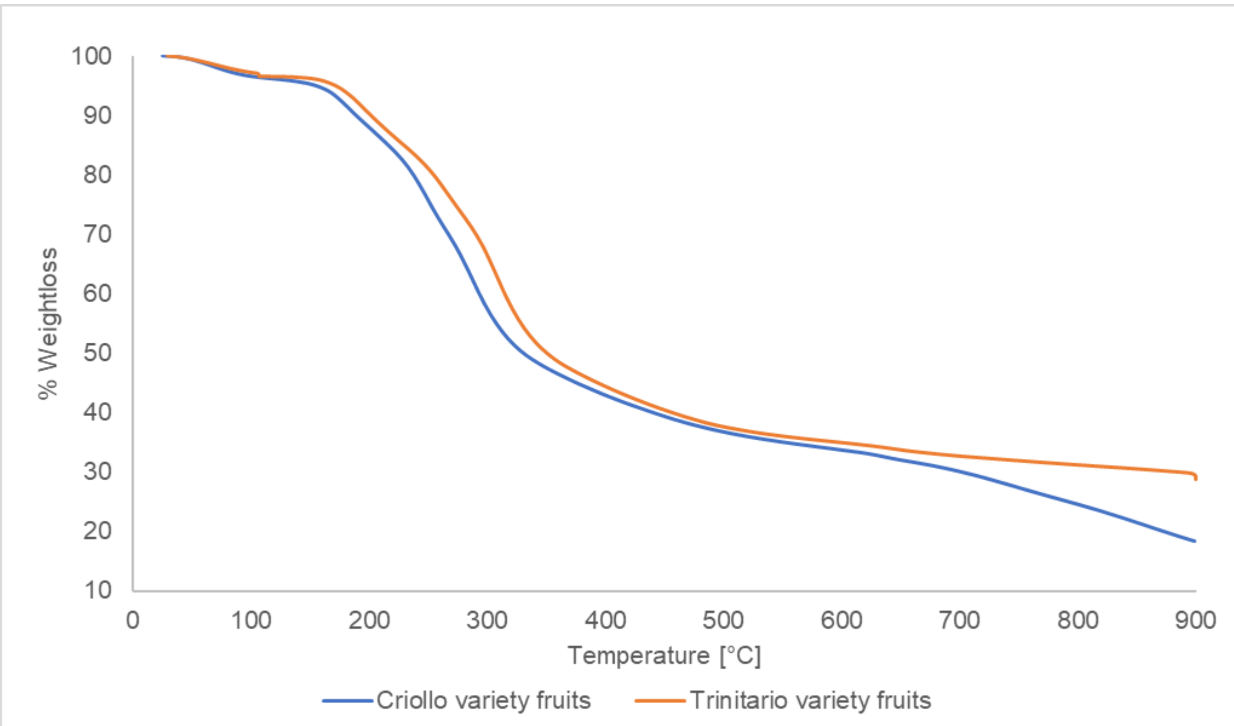



**Figure 21.** TGA of analyzed CPH samples

The content of hemicellulose (52.1%), cellulose (23.7%) and lignin (16.5%) were determined following AOAC 2002.4 and 973.18. 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.

The total potassium determined by atomic absorption was 2795 mg/100g. The physicochemical characterization of CPH on dry matter basis is summarized in **Table 12**. The results obtained for most of the parameters are within the ranges reported by other authors as it is shown previously in **Table 1**.

**Table 12**

Physicochemical characterization of CPH

| Parameter | Value | Method |
|---|---|---|
| Moisture, % | 3.6 | ISO 18134-3:2015 |
| Volatile matter, % | 72.9 | EN ISO 18123:2015 |
| Ash, % | 8.5 | EN ISO 18122:2015 |
| Fixed carbon, % | 15 | By subtracting |
| Hemicellulose, % | 52.1 | Van Soest (AOAC 2002.4) |
| Cellulose, % | 23.7 | Van Soest (AOAC 973.18) |
| Lignin, % | 16.5 | Van Soest (H2SO4) |
| K, mg/100g | 2795 | SM 3111B |

**Table 12** indicates that the quantity of fixed carbon, cellulose, and potassium present in CPH suggests the potential for obtaining activated carbon, cellulose, and potassium hydroxide from this biowaste.

Scanning Electron Microscopy (SEM) with EDX analysis carried out on CPH samples detected elements such as magnesium and calcium in addition to potassium. SEM-EDX analysis was also carried out on the ashes obtained from CPH and additional elements such as silica, phosphorus, sulfur, and copper were detected in minor amount. The averaged results are shown in **Table 13.**

**Table 13**

Results of SEM-EDX analysis of CPH and its ashes

| Element | CPH | | Ashes | |
|---|---|---|---|---|
| | Average w/w %* | σ | Average w/w %* | σ |
| C | 53.4 | 1.5 | 21.1 | 6.1 |
| O | 37.7 | 0.6 | 37.6 | 1.9 |
| K | 7.6 | 0.2 | 32.9 | 3.8 |
| Mg | 0.8 | 1.2 | 2.7 | 0.4 |
| Ca | 0.5 | 0.4 | 2.9 | 1.8 |
| Si | 0.0 | 0.0 | 0.7 | 0.0 |
| P | 0.0 | 0.0 | 0.5 | 0.1 |
| S | 0.0 | 0.0 | 1.5 | 0.6 |
| Cu | 0.0 | 0.0 | 0.3 | 0.2 |

* The average corresponds to three readings performed on each sample. The sample corresponds to the 50-50 mixture of the two varieties analyzed.

The SEM analysis of the ashes obtained from CPH indicates a relative significant amount of potassium, which may exist in the form of oxide or carbonate (Sinaga et al., 2018). This finding suggests that there is a significant potential to extract potassium hydroxide via leaching, with smaller amounts of calcium and magnesium hydroxide.

**Figure 22** displays the structure of the milled CPH as observed through SEM images magnified to x2000. The observation of rigid and fibrous structures composed of lignocellulosic components reveals a small surface area. SEM images of the CPH ashes (**Figure 23**) shows rough and heterogeneous surface with some non-uniform porosity.

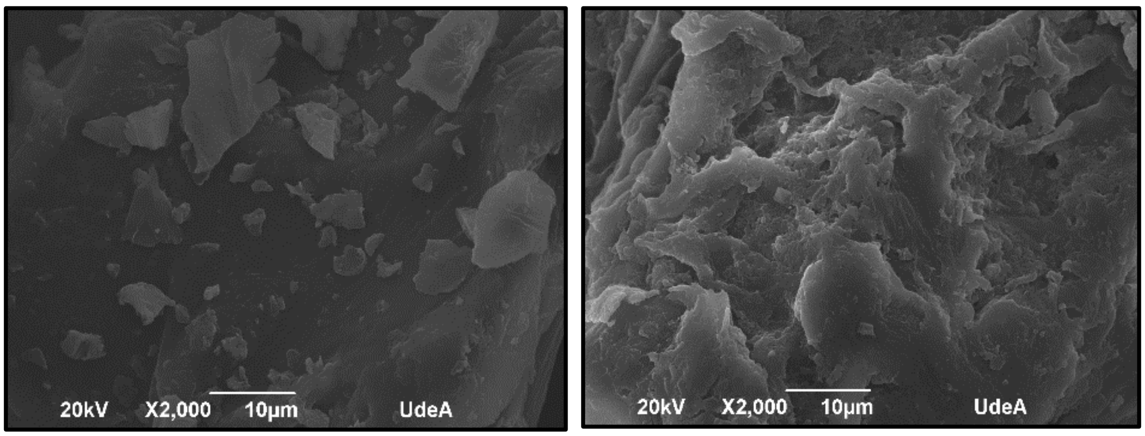



**Figure 22.** SEM images of the analyzed CPH

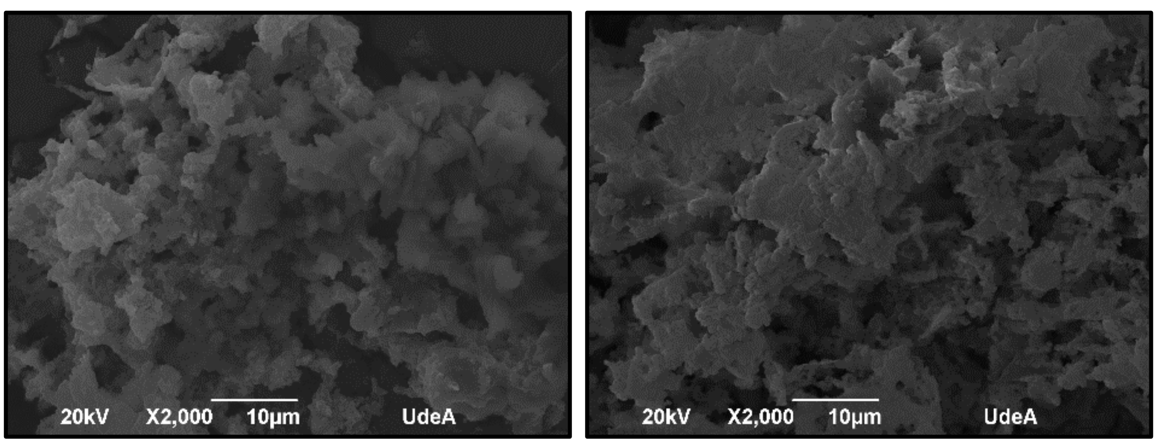



**Figure 23.** SEM images of the analyzed CPH ashes

Based on the data collected from *Héroes del cultivo* Association (**Appendix A**), Lime is the main raw material required for growing organic cocoa as shown in **Table 14.** The number of inputs and outputs of inventory was calculated per one cultivated hectare for the first semester of the year 2022 and projected for the entire year.

**Table 14**

Life cycle inventory data result of organic cocoa production

| Item | Amount | Unit |
|---|---|---|
| *Input* | | |
| Supermagro | 14 | L/ha |
| Lime | 146.7 | kg//ha |
| Gasoil | 44 | L/ha |
| Jute bag | 1.1 | kg/ha |
| Water rain | 77500 | $m^3$/ha |
| *Output* | | |
| Dry cocoa beans | 117 | kg/year.ha |
| Cocoa pod husk | 1214 | kg/year.ha |
| Mucilage | 332 | kg/year.ha |

### 4.1.2. Life cycle inventory analysis of activated carbon production from CPH

The yield obtained to produce activated carbon from non-pretreated CPH was 3.6 %. **Table 15** relates the amount of energy and materials utilized in the laboratory for activated carbon production, along with the corresponding outputs generated. This result is based on the transformation process outlined in section 3.2.2, which covers activated carbon production from CPH.

**Table 15**

Life cycle inventory data result to produce activated carbon from CPH

| Item | Amount | Unit |
|---|---|---|
| *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 | | |
| CPH drying (pre-treatment) | 2.1 | kWh |
| CPH grinding (pre-treatment) | 0.026 | kWh |
| Chemical activation | 0.260 | kWh |
| Drying of CPH activated | 1.375 | kWh |
| Pyrolysis | 1.575 | kWh |
| Drying of activated carbon | 1.0 | kWh |

| | | |
|---|---|---|
| *Output* | | |
| Activated carbon | 1.55 | g |
| Liquid waste | 71.5 | mL |

#### 4.1.3. Life cycle inventory analysis of potassium hydroxide production from CPH

The yield obtained to produce potassium hydroxide from non-pretreated CPH was 0.73 %. **Table 16** relates the amount of energy and materials utilized in the laboratory for potassium hydroxide production, along with the corresponding outputs generated. This result is based on the transformation process outlined in section 3.2.3, which covers potassium hydroxide production from CPH.

**Table 16**
Life cycle inventory data result to produce KOH from CPH

| Item | Amount | Unit |
|---|---|---|
| *Input* | | |
| Cocoa pod husk | 178 | g |
| Deionized water | 51 | mL |
| $Ca(OH)_2$ | 0.54 | g |
| Electricity | | |
| CPH drying (pre-treatment) | 2.1 | kWh |
| CPH grinding (pre-treatment) | 0.026 | kWh |
| Calcination | 0.525 | kWh |
| Leaching | 0.280 | kWh |
| Evaporation to obtain $K_2CO_3$ | 0.280 | kWh |
| Caustification | 0.140 | kWh |
| Evaporation to obtain KOH | 0.280 | kWh |
| *Output* | | |
| Potassium hydroxide (85%) | 1.3 | g |
| $CaCO_3$ | 1.2 | g |
| Solid waste | 0.9 | g |

#### 4.1.4. Life cycle inventory analysis of cellulose production from CPH

The yield obtained to produce cellulose from non-pretreated CPH were 4.5 % and 8.7% by alkaline and autohydrolysis treatment respectively. **Table 17** and **18** relates the amount of energy and materials utilized in the laboratory for cellulose unbleached production, along with the corresponding outputs generated. This result is based on the transformation process outlined in section 3.2.4, which covers cellulose production from CPH by both methodologies.

**Table 17**

Life cycle inventory data result of CPH transformation to cellulose by alkaline treatment

| Item | Amount | Unit |
|---|---|---|
| *Input* | | |
| Cocoa pod husk | 71.2 | g |
| Sodium hydroxide (NaOH) 50% | 8 | g |
| Deionized water | 398.6 | mL |
| Electricity | | |
| CPH drying (pre-treatment) | 2.1 | kWh |
| CPH grinding (pre-treatment) | 0.026 | kWh |
| Alkali treatment | 0.280 | kWh |
| Drying | 1 | kWh |
| *Output* | | |
| CAT | 3.2 | g |
| Liquid waste | 412.5 | mL |

**Table 18**

Life cycle inventory data result of CPH transformation to cellulose by autohydrolysis

| Item | Amount | Unit |
|---|---|---|
| *Input* | | |
| Cocoa pod husk | 71.2 | g |
| Deionized water | 130 | mL |
| Electricity | | |
| CPH drying (pre-treatment) | 2.1 | kWh |
| CPH grinding (pre-treatment) | 0.026 | kWh |
| Autohydrolysis | 0.1 | kWh |
| Drying | 1 | kWh |
| *Output* | | |
| CAH | 6.2 | g |
| Liquid waste | 100 | mL |

## 4.2. Life Cycle Impact Assessment (LCIA) and interpretation

### 4.2.1. LCIA of organic cocoa production

**Table 19** shows the LCIA result of organic cocoa production for the two scenarios: one where 1 kg of CPH (wet weight) is disposal in open field, and the other where the CPH is utilized as a co-product to obtain value-added products.

**Table 19**
LCIA result of organic cocoa production with different allocation procedure

| Impact category ($CF_m$) | Unit | Organic cocoa production with CPH disposal in open field | Organic cocoa production with CPH as a co-product |
|---|---|---|---|
| Climate change (GWP) | kg $CO_2$ eq | 1.160E-00 | 2.120E-01 |
| Human toxicity: cancer (HTPc) | kg 1.4-DCB | 3.410E-03 | 1.590E-03 |
| Terrestrial acidification (TAP) | kg $SO_2$ eq | 2.930E-04 | 1.780E-04 |
| Freshwater eutrophication (FEP) | kg P eq | 5.580E-03 | 9.600E-04 |
| Terrestrial ecotoxicity (TETP) | kg 1.4-DCB | 1.800E-01 | 1.380E-01 |
| Freshwater ecotoxicity (FETP) | kg 1.4-DCB | 2.570E-02 | 5.420E-03 |
| Marine ecotoxicity (METP) | kg 1.4-DCB | 3.520E-02 | 7.480E-03 |
| Mineral resource scarcity (SOP) | kg Cu eq | 1.790E-04 | 1.390E-04 |
| Fossil resource scarcity (FFP) | kg oil eq | 4.540E-02 | 3.520E-02 |
| Water consumption (WCP) | $m^3$ | 8.620E-04 | 6.680E-04 |

**Table 19** shows that when the CPH is disposed of in open field (considered as biowaste), the environmental impact increases for all evaluated categories. The $CF_m$ that has a notable impact is the Global warming potential (GWP), which is 81.7% higher when the CPH is considered as biowaste that degrades in the open field compared with the scenery when CPH is regarded a co-product that can be used as raw material to be transformed into value-added products. The categories that exhibit a significant difference between the two scenarios are: FEP, FETP, METP, HTPc and TAP with a reduction of 82.8%, 78.9 %, 78.8%, 53.4% and 39.2% respectively. The categories that are least affected by the quantity and allocation of CPH are: TETP, FFP, WCP and SOP with 23.3%, 22.5%, 22.5% and 22.3% respectively.

The impact contribution for each of the scenarios is shown in **Figures 24** and **25**. For both evaluated scenarios, the biowaste is the main contributor to the GWP impact. When the biowaste degradation occurs, resulting in the production of greenhouse gases, primarily carbon dioxide and methane. Biowaste contributes to HTPc mainly through its heavy metal and dioxins emissions. Biowaste degradation also generates leachates that cause soil alterations such as acidification (TAP). These leachates eventually end up into bodies of water, leading to adverse effects including eutrophication (FEP) and ecotoxicity (FETP and METP)(Güereca et al., 2006). When CPH is not included as part of the biowaste generated during organic cocoa production, its contribution decreases in the impact categories, as the amount of biowaste significantly reduces.

Supermagro is a proprietary biofertilizer with a barely noticeable contribution in the TETP (21%) and SOP (8.4%) categories. The formulation contains various compounds, including minerals in the form of salts such as copper sulfate, which is the major contributor to the Supermagro in TETP due to the use of sulfuric acid during its production. Furthermore, it is observed that the biofertilizer made only a minimal contribution (less than 5%) to any other categories in the two evaluated scenarios. This is because the biofertilizer is composed of a high proportion of natural materials that are readily available on the farm, such as cow manure, raw milk, and molasses, among others (Robinson Tapiero, personal interview, 24th October 2022).

In organic farming practices, the use of lime during the vegetative growth stage is common, in addition to the use of biofertilizers. The production of lime requires a mining extraction of limestone, followed by its crushing, calcination, and hydration. These processes contribute significantly to the TETP, HTPc, WCP, TAP categories, and even more to the mineral resource scarcity (SOP) due to the mining extraction required.

To produce organic cocoa, pest and weed control is performed mechanically with chainsaw. As a result, gasoil used for the chainsaw is an important contributor in certain impact categories, particularly TAP, FFP and HTPc. Water is a key resource in the process of transforming jute fibers into bags, making its greatest contribution to the WCP category.

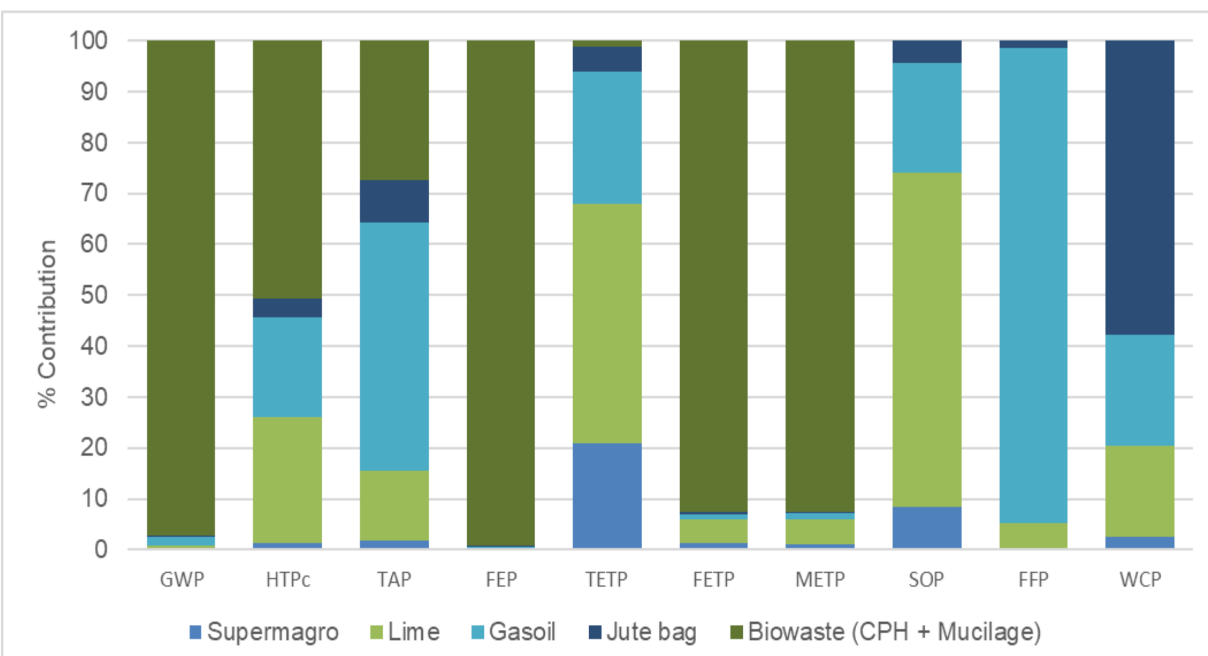



**Figure 24.** LCA contribution results for organic cocoa production with CPH disposal in open field

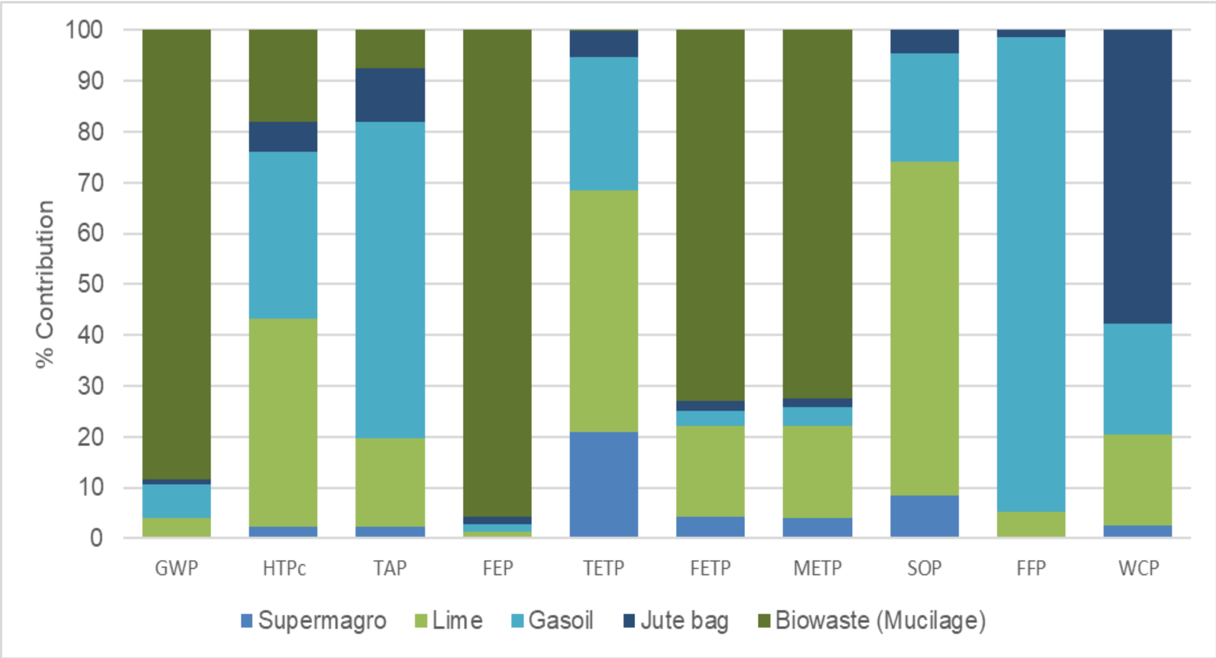



**Figure 25.** LCA contribution results for organic cocoa production with CPH as co-product

### 4.2.2. Comparative LCIA of CPH transformation processes

**Table 20** presents the comparative characterization of life cycle impact assessment for the evaluated processes and the CPH disposal in open field. The results reveal that among the transformation processes to use CPH, the production of KOH exhibits the most favorable environmental performance.

**Table 20**

Comparative LCIA (characterization) of CPH transformation into value-added products

| Impact category ($CF_m$) | Unit | AC | CAT | CAH | KOH | CPH disposal in open field |
|---|---|---|---|---|---|---|
| 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 |

The overall environmental impacts (normalized) of value-added products obtained from CPH, as well as the disposal of CPH in an open field are illustrated in **Figure 26**. The normalized total scores of life cycle impact assessment, for each evaluated scenario, decreased in the following order: 0.173 to produce activated carbon, 0.058 to produce CAT, 0.053 to produce CAH, 0.013 to produce KOH, and 0.011 for CPH disposal in open field.

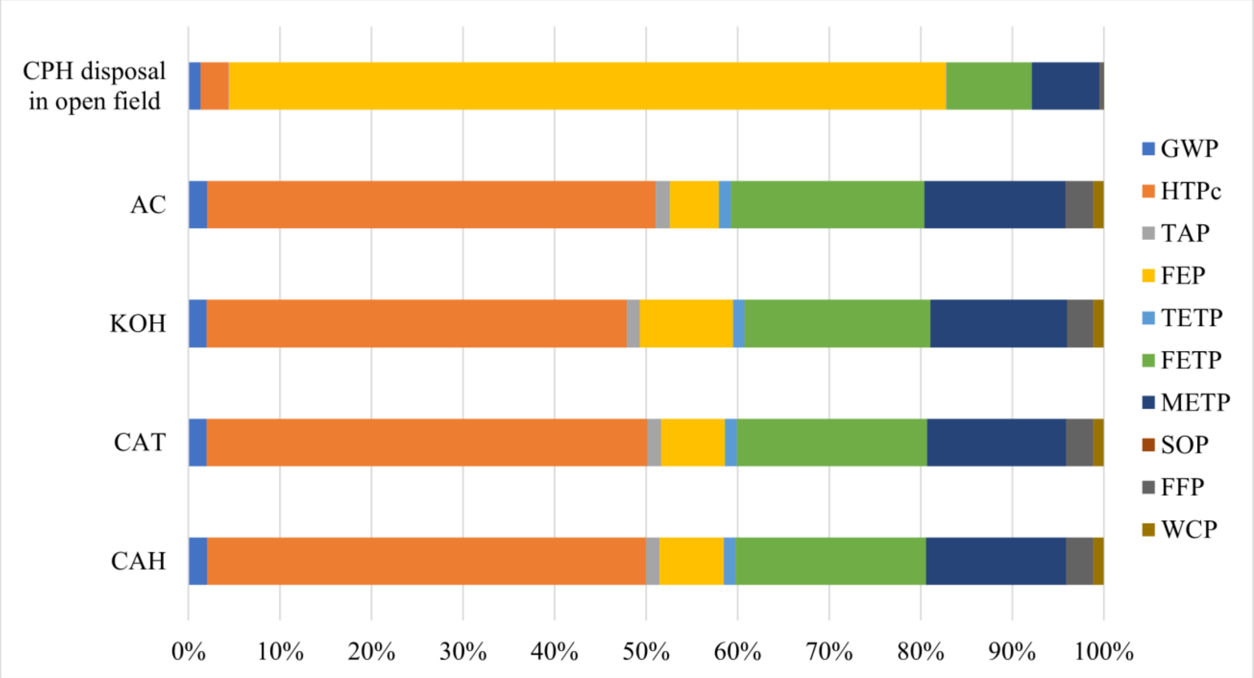



**Figure 26.** Comparative impact assessment (normalized) of value-added products and CPH disposal in open field

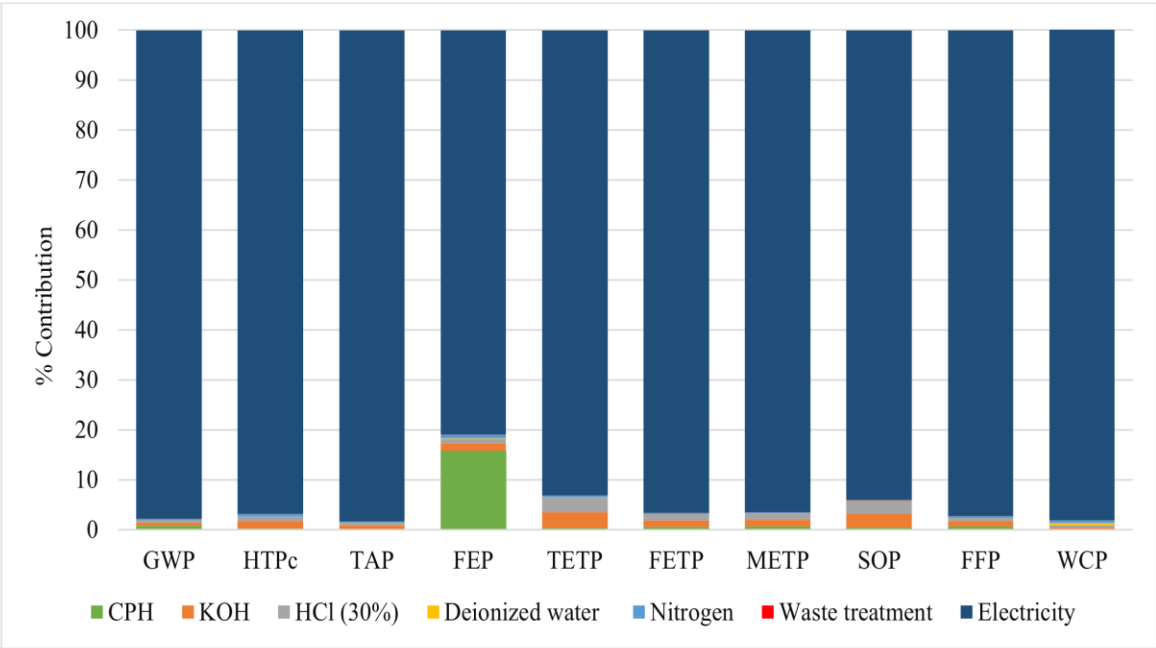
The results show that for the scenario where CPH is disposed of in an open field, the highest impact value corresponds to FEP (78.4%). This is attributed to the degradation of the large amount of biomass, resulting in the generation of leachates that end up in bodies of water, leading to adverse effects including eutrophication and ecotoxicity (Güereca et al., 2006). For the transformation processes of the CPH, the categories with the most significant impact are HTPc, FETP and METP. The production of activated carbon accounts for 49.1% (HTPc), 21.1% (FETP), and 15.5% (METP). In the case of KOH production, the contributions are 45.9% (HTPc), 20.3% (FETP), and 14.9% (METP). Similarly, to produce cellulose using either of the two methodologies, the values 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 (2%), TAP (1.5%), TETP (1.3%), and WCP (1.2%) across all transformation processes. Finally, SOP category has a negligible contribution to the overall environmental assessment.

#### 4.2.3. Impact contribution of CPH transformation processes

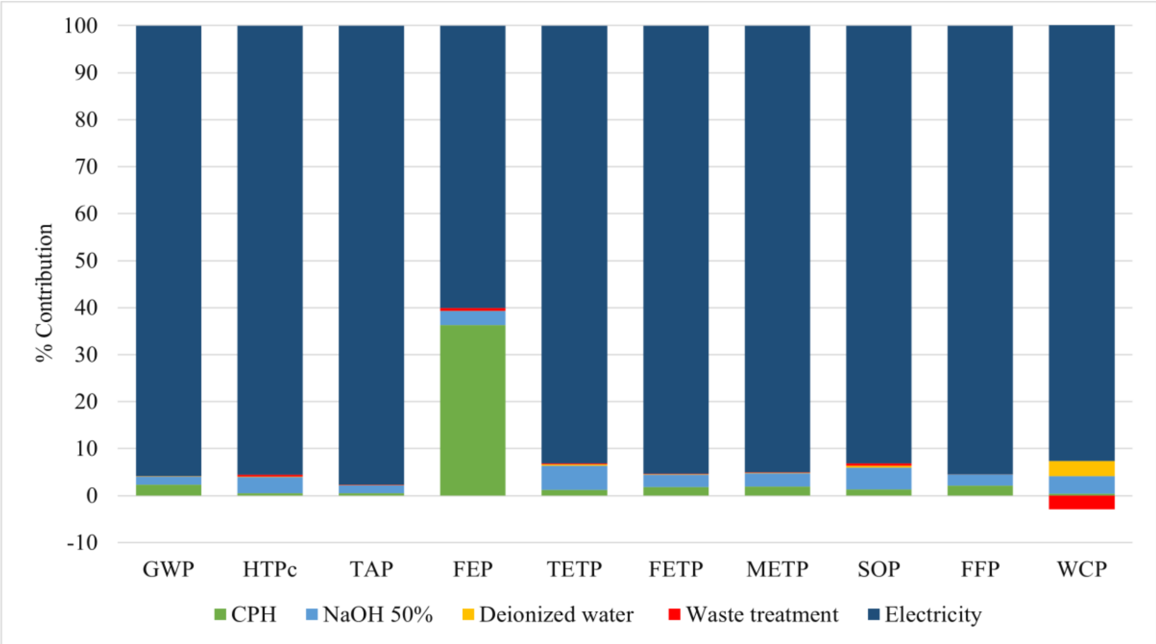
The impact contribution analysis allows to identify the hotspots of the environmental assessment for each of the analyzed transformation processes of CPH and propose alternatives for environmental improvement of the processes. The impact contribution of the CPH transformation processes is shown in **Figure 27a, 27b, 27c** and **27d**. 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 energy consumed is considered from the generation system in Colombia, with 62% originating from hydroelectric plants, 29% from thermal plants, and the remaining 9% from solar and wind sources (UPME, 2023). Thermal plants require coal and natural gas, and the production and utilization of these materials result in the emission of greenhouse gases, contributing to the GWP, HTPc, TAP categories. Sustaining the energy transmission network demands a substantial quantity of copper, and its production leads to soil and water contamination, thereby contributing to the TEP, TETP, FETP, and METP categories. In other impact categories, the utilization of water in hydroelectric plants influences the availability of water resources, contributing to the WCP category. The use of gas in thermoelectric plants affects the availability of fossil resources, contributing to the FFP category. Lastly, the use of steel and copper alloy materials in energy transmission and transformation substations influences mineral availability, contributing to the SOP category.

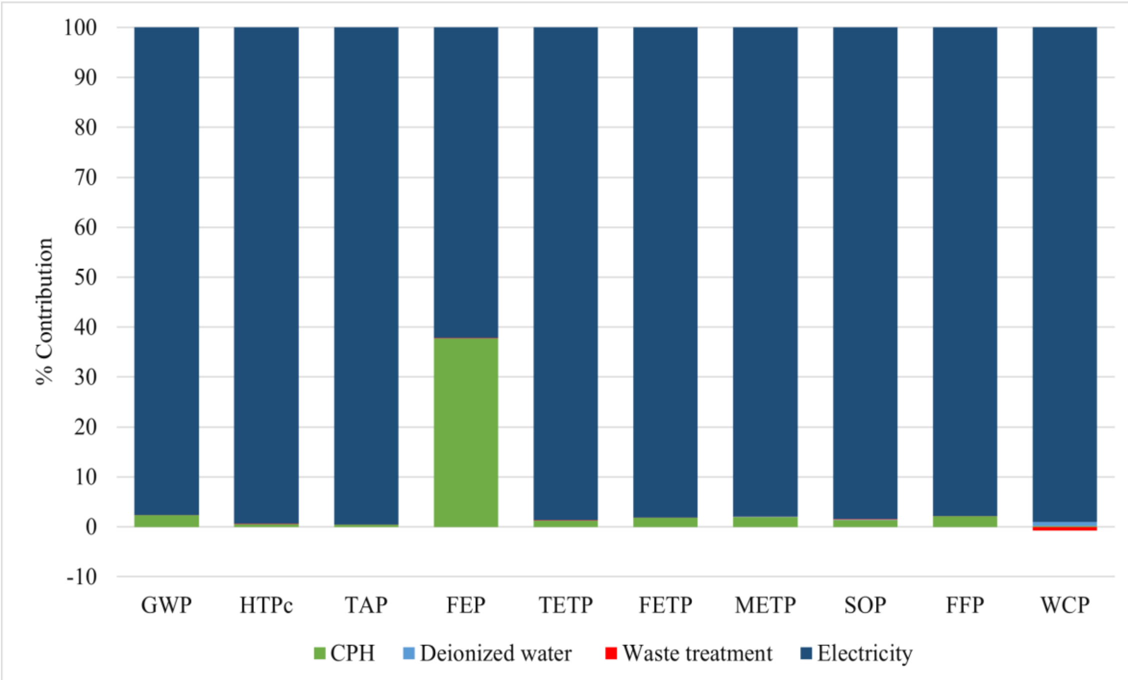
The CPH becomes a notable contributor in FEP category to produce activated carbon (15.8%), cellulose by alkaline treatment (36.3%), cellulose by autohydrolysis (37.7%) and KOH (59.3%). This contribution can be associated to the nutrients and minerals that eventually end up in water bodies during cocoa production where the CPH is generated.



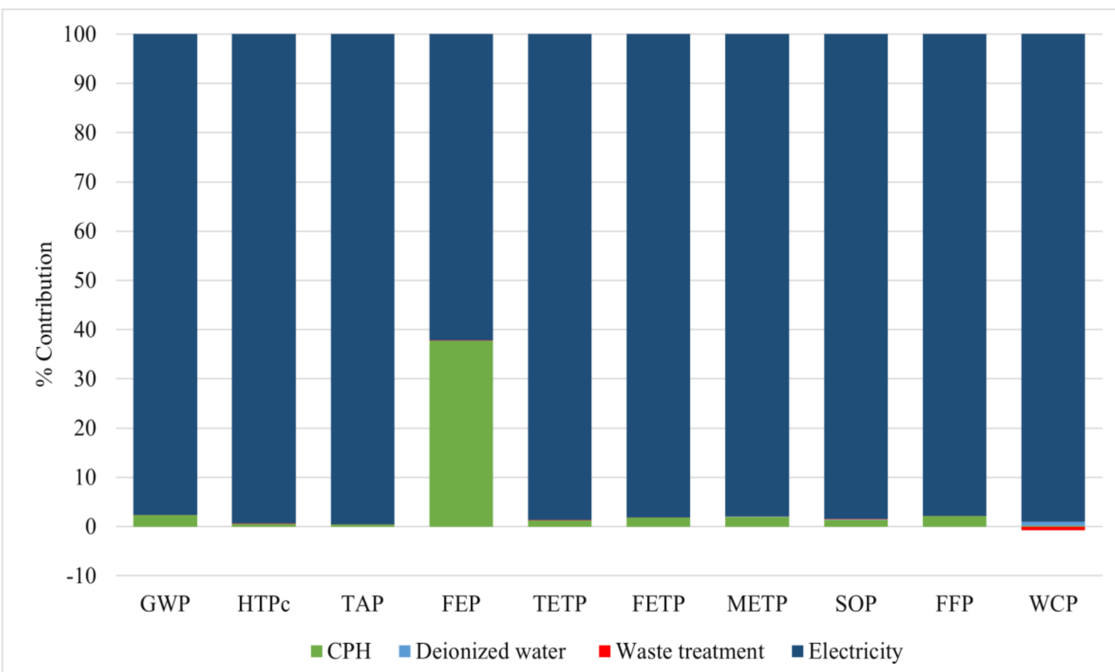

a)




b)



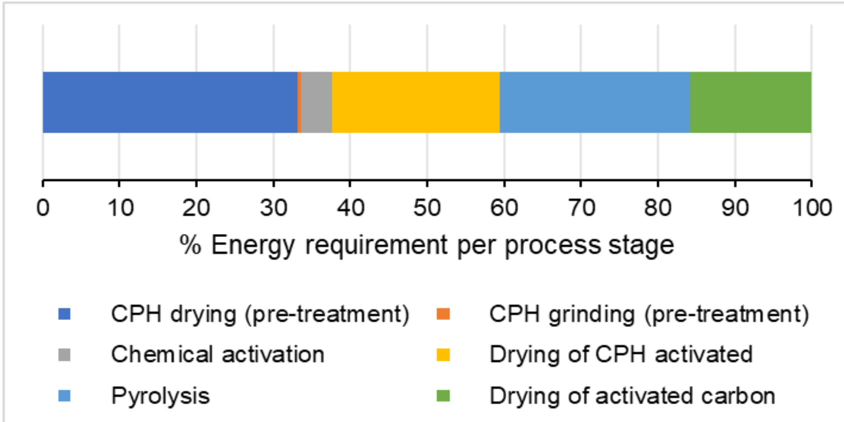

c)



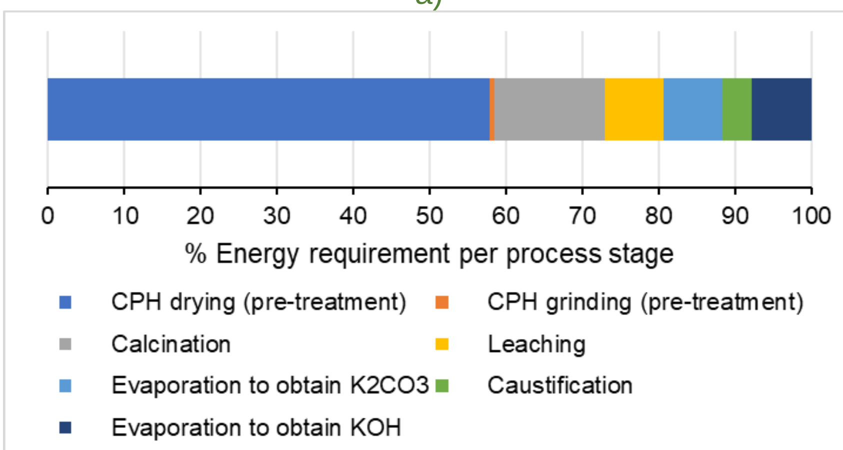

d)

**Figure 27.** LCIA contribution by transformation processes to produce a) AC, b) CAT, c) CAH, d) KOH

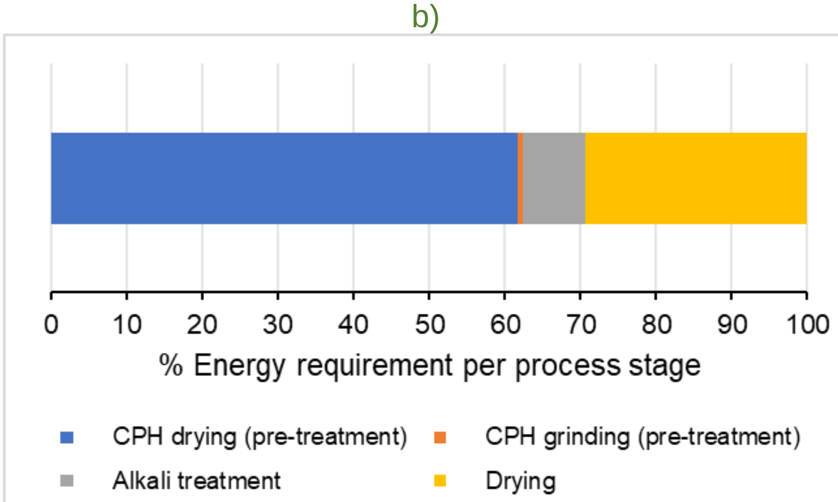
**Figure 28** shows the contribution of electricity, identified as the predominant factor across all evaluated CFm (See **Figure 27**), throughout the stages of the transformation process. This representation corresponds to the energy analysis inventory previously presented in subsections 4.1.2, 4.1.3, and 4.1.4.




a)




b)

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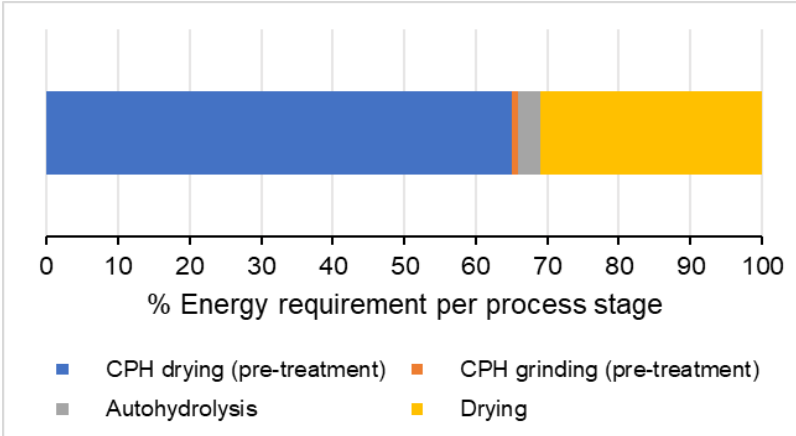


d)

**Figure 28.** Electricity contribution per process stage to produce a) AC, b) CAT, c) CAH, d) KOH

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 the transformation processes is the pyrolysis performed at 500°C for 3 h to produce activated carbon, the calcination at 650°C for 1 h to produce potassium hydroxide, and the drying stages. To produce cellulose through alkaline treatment, a positive contribution to the environment is observed in the WCP category; a 2.9% credit was obtained 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% credit) 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 number of reagents are used, they are non-toxic and are used in small quantities.

#### 4.2.4. 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 source. The baseline (BL) scenario corresponds to the outcomes discussed in section 4.2.2, 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.

**Figure 29** 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 pre-treatment 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 obtained as a co-product during the production of potassium hydroxide, with the impact allocation distributed between the two products. 52% for KOH and 48% for $CaCO_3$.

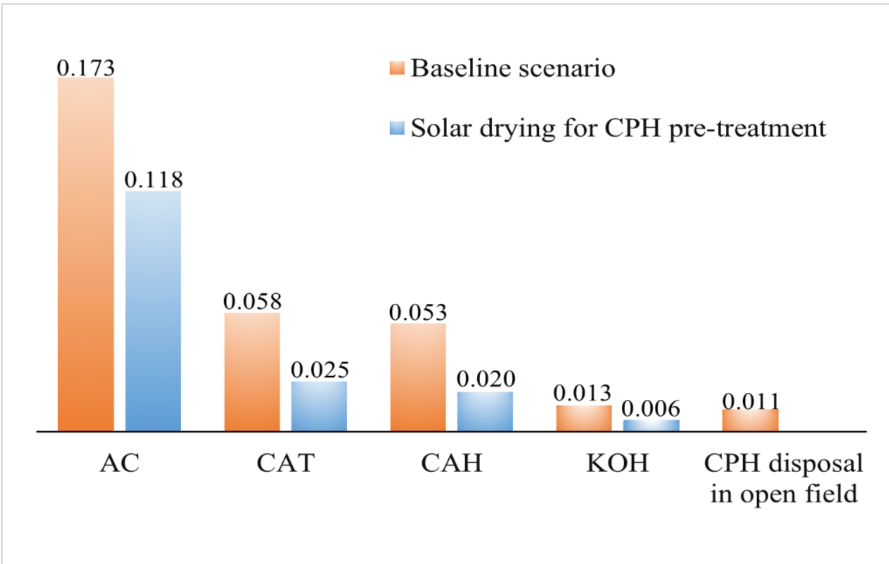


**Figure 29.** Normalized total scores from the sensitivity analysis for transformation processes

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). **Figure 30** 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 reduction in impact (solid line in **Figure 30**) 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 4.2.2. This reinforces the finding that CPH plays an important role in the contribution to the FEP impact.

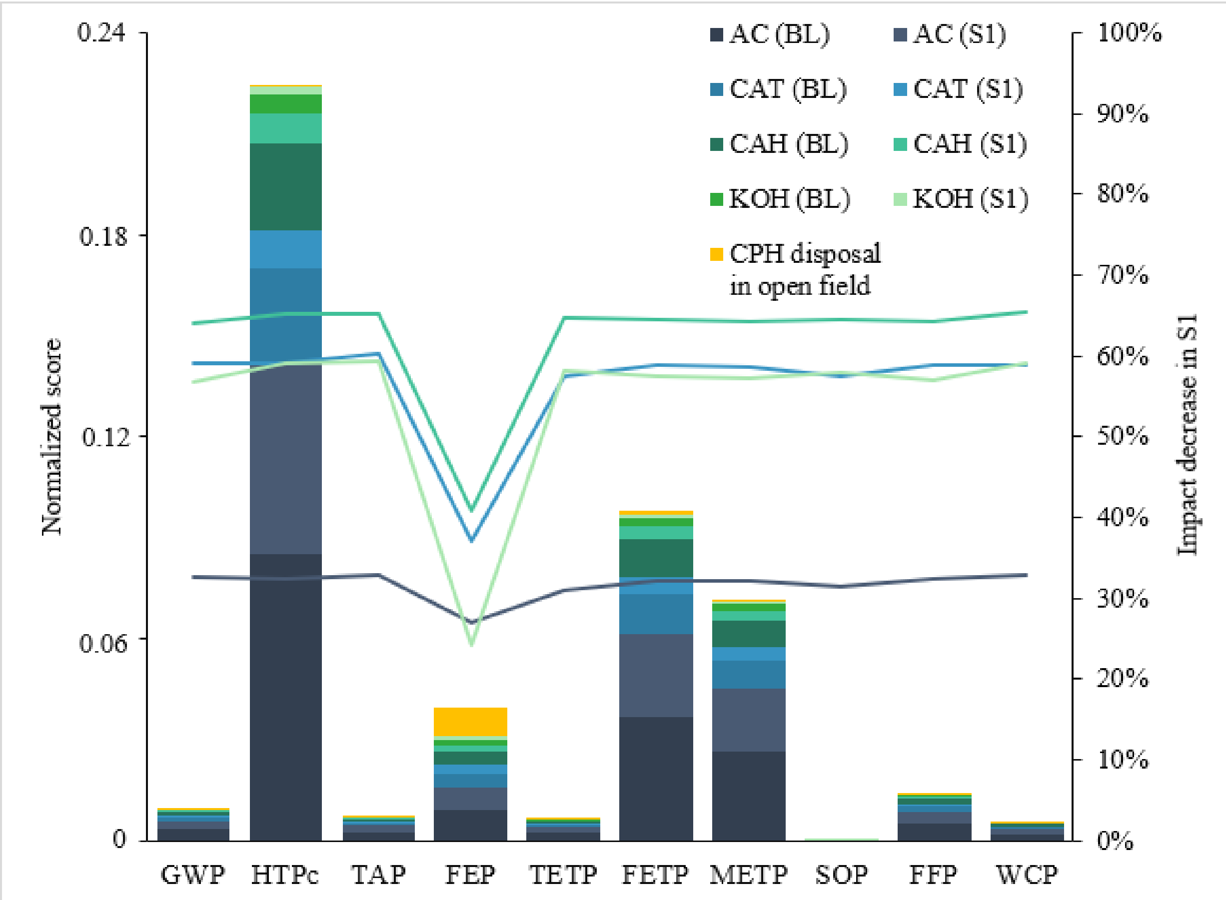


**Figure 30.** Normalized score and percentage decrease from sensitivity analysis. *The columns represent the normalized score for each product and scenario. The solid line represents the impact decrease in S1 with respect to BL.*

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.

### 4.3. Characterization of value-added products obtained from CPH

Several tests were conducted to determine the physical-chemical properties of the obtained products, characterize them, and evaluate their suitability for industrial applications.

### 4.3.1. Activated carbon

The yield obtained with the transformation process employed was 3.6% in relation to untreated CPH, and 25.8% regarding the treated CPH (dried and ground). The resulting product is show in **Figure 31.**

**Figure 31.** A*ctivated carbon obtained from CPH (Author)*

SEM-EDX semiquantitative analysis carried out on activated carbon obtained indicate that the material contains mainly carbon (89%), oxygen (7.8%) and a small amount of Mg (0.7%), Cl (1.0%), and K (1.5%) minerals (See **Table 21**). 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 (Cruz, 2012; Tejada et al., 2017).

**Table 21**
Results of SEM-EDX analysis of activated carbon from CPH

| Element | Average w/w %* | σ |
|---|---|---|
| C | 89.0 | 0.99 |
| O | 7.8 | 2.25 |
| Mg | 0.7 | 0.35 |
| Cl | 1.0 | 0.68 |
| K | 1.5 | 0.64 |

** The average corresponds to three readings performed on each sample.*

SEM images of activated carbon correspond to **Figure 32** a), b). The micrographs indicate the presence of abundant pores and exhibit a morphology characterized by its regular shape with nested cavities and spongy surface. The porous structure comprises of randomly oriented microspores.

a) b)

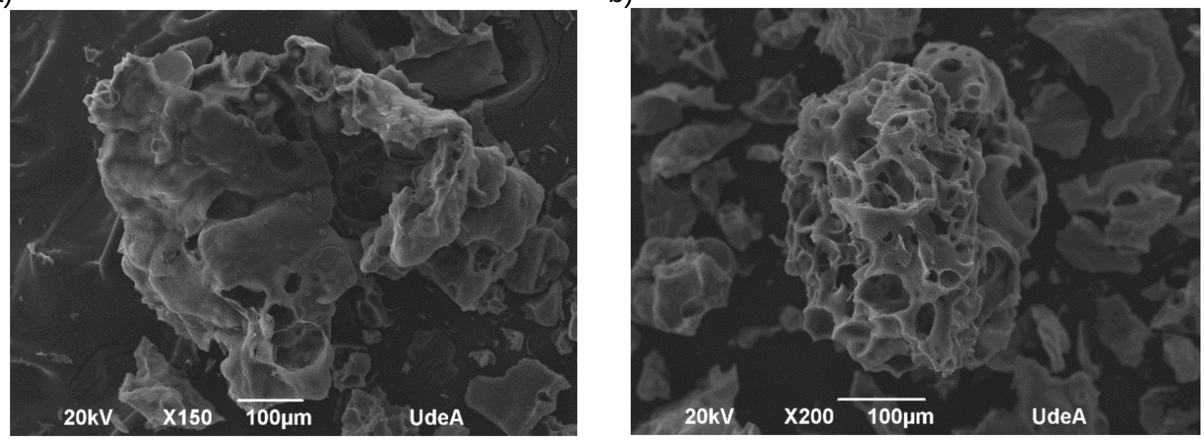


**Figure 32.** SEM images of activated carbon from CPH a)X150, b)X200 (Author)

The isotherm was carried out in the pressure interval 0.1 – 0.998, adsorption and desorption (50 points minimum). The results obtained are shown in **Table 22** and **Figure 33.**

**Table 22**
Structural properties of activated carbon

| **Property** | |
|---|---|
| BET surface area ($m^2/g$)[a] | 467.5156 |
| Micropore surface area ($m^2/g$)[b] | 370.6721 |
| Total pore volume ($cm^3/g$)[c] | 0.228138 |
| Micropore volume ($cm^3/g$)[d] | 0.142858 |
| Pore Width (nm)[e] | 1.093827 |

[a] BET surface area based on the relative pressure (P/P0) ranging from 0.05 to 0.4.
[b] Micropore area by t-plot method
[c] Total pore volume obtained at relative pressure of about 0.99
[d] Micropore volume by t-plot method
[e] Estimated by t-plot method (See **Figure 33**)

The structural properties obtained are similar to 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).

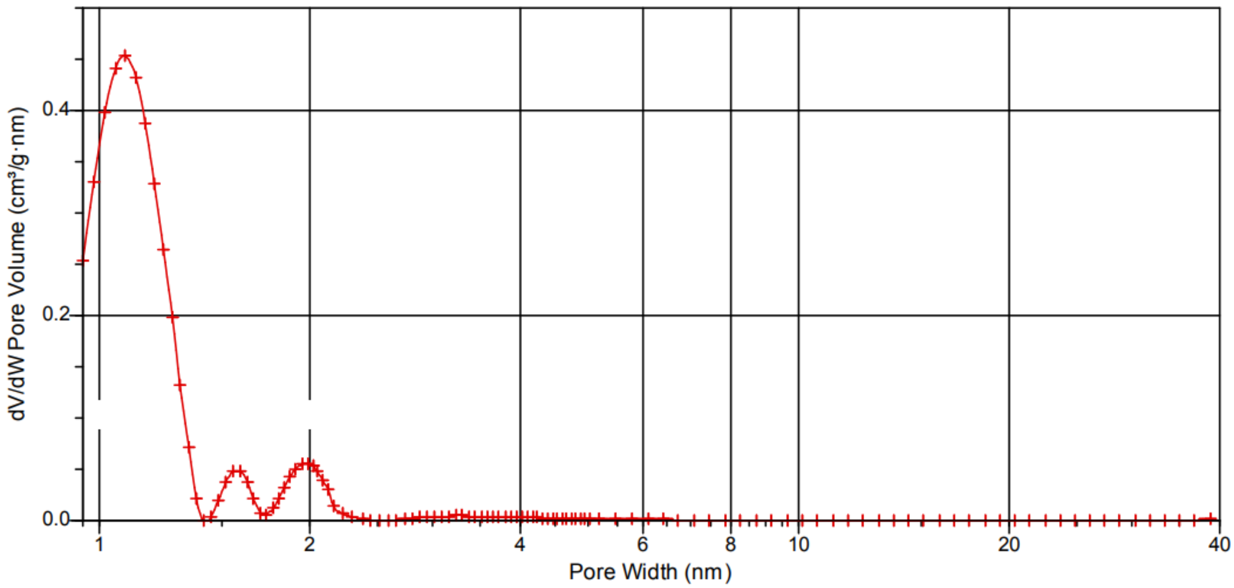


**Figure 33.** Plot dv/dw pore volume vs. pore width

**Figure 33** reveals that the highest area under the curve is associated with the 1.0938 nm pore amplitude peak, followed by two smaller areas of the 1.5942 nm and 1.9874 nm pore amplitude peaks. This indicates that the activated carbon porosity primarily comprises micropores with a few mesopores. The findings in the **Table 22** support this observation, with 79.3% of the surface area and 62.6% of the total volume corresponding to micropores (Lowell et al., 2004).

The characteristics of the activated carbon obtained show 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). These results demonstrate that activated carbon from CPH could be an excellent precursor for the development of adsorbents for water treatment.

### 4.3.2. Potassium hydroxide

The yield obtained with the transformation process employed was 0.73% in relation to untreated CPH, and 5.1% regarding the treated CPH (dried and ground). These results are higher than those obtained by Ofori et al. (2017), where the yield was 0.3% for untreated CPH and 1.57% regarding the treated CPH (dried and ground). The resulting product has a crystalline white appearance as shown in **Figure 34** and is odorless.

**Figure 34.** Potassium hydroxide obtained from CPH (Author)

The potassium hydroxide content, determined through acid-base titration, indicates a purity of 84.16% of KOH obtained from CPH. The reported purity of commercial KOH by the provider (MERCK, Reference 221473, ACS reagent, ≥85% pellets) is stated as being ≥85%. These results highlight the effective performance of the transformation process utilizing CPH as a source of potassium.

### 4.3.3. Cellulose

The yields obtained in the production of unbleached cellulose through alkaline treatment and autohydrolysis are shown in **Table 23**.

**Table 23**
Cellulose production yields from CPH

| | Yield from non-pretreatment CPH (%) | Yield from pre-treated CPH (%) |
|---|---|---|
| CAT | 4.5 | 32.3 |
| CAH | 8.7 | 61.7 |

The product obtained is brown in color, odorless, with powdery and fibrous appearance as shown in **Figure 35**.

a) b)

**Figure 35.** Unbleached cellulose obtained from CPH a) Cellulose by alkaline treatment, b) Cellulose by autohydrolysis (Author)

The α-cellulose content of the pulps was determined using the TAPPI T 203 standard, leading to a purity of 85% and 63.5%, respectively, for the pulp obtained from alkaline treatment and autohydrolysis. This is consistent with the results of a similar study conducted by Torres et al. (2019). The obtained α-cellulose content implies that this material has potential as a non-wood fiber for use in pulp and paper production (Torres, 2019).

## 5. Conclusions and Recommendations

The LCA works as a valuable tool for evaluating the environmental loads of agricultural activities, enabling decisions to be made towards sustainable development. Upon evaluating the life cycle impact of CPH generated during the production of organic cocoa, it becomes evident that the environmental impact is significantly reduced when this bio-waste is considered a co-product, capable of producing value-added products, as opposed to being disposed of in open fields where it decomposes organically. The impact categories that exhibit a significant difference between the two scenarios are FEP, GWP, FETP, METP with a reduction of 82.8%, 81.7%, 78.9 % and 78.8% respectively, since the main contributors to these categories are the biowaste consisting of CPH and mucilage. It is also observed that in organic cultivation practices, where insecticides and pesticides are avoided and mechanical control is employed instead, the use of gasoil for chainsaws significantly contributes to impacts such as FFP, TAP, and HTPc. On the other hand, the use of lime contributes to almost all evaluated impact categories, highlighting the need for technical evaluation and optimization of its application in this agricultural activity.

The results of the inventory analysis for the CPH transformation show that the production of activated carbon exhibits the highest energy requirement compared to other processes. On the other hand, the process of obtaining cellulose through alkaline treatment evideced the highest water requirement and generates the largest volume of liquid waste that needs treatment. Notably, the production of KOH is unique as it yields calcium carbonate as a co-product. Among these processes, the inventory resulting from the cellulose production process through autohydrolysis is the most compact in terms of the number of inputs and outputs.

Considering that there are many potential ways for the utilization of CPH, using LCA to evaluate each scenario is an excellent tool for the decision-making process, focusing on optimal environmental performance. The LCIA of the four transformation processes indicates that the production of KOH exhibits the highest environmental performance, 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 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, attributed to the release of mineral nutrients that ultimately leach into freshwater bodies.

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. Modifying the drying method of CPH for pretreatment, incorporating natural sun drying, and eliminating the energy demand at this process stage, the normalized total score decreases significantly. There is a reduction of 62.3% in the production of CAH, followed by 56.9% in the production of CAT, 53.8% in the production of KOH, and, finally, a 31.8% decrease in the production of activated carbon. It also highlights that, under this consideration, the production of KOH has the lowest environmental impact when compared to the conventional disposal of CPH in 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 $CaCO_3$.

The characterization of the products obtained from CPH shows that activated carbon, potassium hydroxide, and cellulose have favorable properties, making them suitable for various potential applications. Activated carbon exhibits good adsorbent properties, rendering it suitable for application in aqueous medium and catalyst preparation. Potassium hydroxide proves valuable in the production of cleaning agents, such as soaps and detergents. Obtained cellulose from CPH has potential use within the pulp and paper industry.

This study enables the identification of the environmental efficiency of utilizing cocoa production residue (CPH) for KOH production when compared to the environmental impact of traditional disposal methods, such as leaving it exposed in an open field. This insight serves as a base for future research that aims to sustainable optimization of the transformation process used, and/or potentially expanding to large-scale plant production. For cellulose and activated carbon production, this study provides a starting point for process optimization or the exploration of alternative technologies, considering environmentally critical points identified in the transformation processes. Additionally, comparisons of environmental performance can be made with conventional production processes for the considered products, offering essential scientific information to guide decisions regarding economic-industrial development with a focus on sustainability.

For future projects, it is recommended to focus on the optimization of the transformation processes utilized in this study, with the aim of reducing the energy requirements for each process. Additionally, it would be beneficial to explore the integration of renewable energy sources, assessing their potential to enhance the environmental performance.

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# Supplementary Material

## **Appendix A.** Field survey record of organic cocoa production in the Héroes del Cultivo association.

**Table A1**

Field survey record of farm production and requirements for crop establishment period, all of which were carried out using organic practices.

| Farm | Cultivated cocoa area [ha] | Varieties of cocoa fruit | Production. Period: January to June 2022 [kg "cocoa in slime"] | Average "cocoa in slime" harvest yield [kg/year . ha] | Requirements for crop establishment | | | | | | | | | Weed control | | | Shadow and Shape control | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Nursery | Cal [kg/year . ha] | | | | Supermagro Biofertilizer [L/year . ha] | | | | Gasoil [L/year . ha] | | | | |
| | | | | | | 1 year | 2 year | 3 year | 4 year | 1 year | 2 year | 3 year | 4 year | 2 year | 3 year | 4 year | 3 year | 4 year |
| El Recreo | 1 | Criollo, Trinitario, Forastero. | 297 | 594 | Sand seedbeds and farm seeds | 13.3 | 26.7 | 53.3 | 53.3 | 2 | 4 | 4 | 4 | 12 | 12 | 12 | 4 | 4 |
| Buenos Aires | 2.1 | | 234 | 223 | | 13.3 | 26.7 | 53.3 | 53.3 | 2 | 4 | 4 | 4 | 12 | 12 | 12 | 4 | 4 |
| La Primavera | 1.5 | | 760 | 1013 | | 13.3 | 26.7 | 53.3 | 53.3 | 2 | 4 | 4 | 4 | 12 | 12 | 12 | 4 | 4 |
| Oasis Santuario | 2.2 | | 288 | 262 | | 13.3 | 26.7 | 53.3 | 53.3 | 2 | 4 | 4 | 4 | 12 | 12 | 12 | 4 | 4 |
| La Esperanza | 1 | | 418 | 836 | | 13.3 | 26.7 | 53.3 | 53.3 | 2 | 4 | 4 | 4 | 12 | 12 | 12 | 4 | 4 |
| La Cascada | 1 | | 188 | 376 | | 13.3 | 26.7 | 53.3 | 53.3 | 2 | 4 | 4 | 4 | 12 | 12 | 12 | 4 | 4 |
| Las Camelias | 3 | | 480 | 320 | | 13.3 | 26.7 | 53.3 | 53.3 | 2 | 4 | 4 | 4 | 12 | 12 | 12 | 4 | 4 |
| El Porvenir | 1 | | 279 | 558 | | 13.3 | 26.7 | 53.3 | 53.3 | 2 | 4 | 4 | 4 | 12 | 12 | 12 | 4 | 4 |
| El Retiro | 4.8 | | 936 | 390 | | 13.3 | 26.7 | 53.3 | 53.3 | 2 | 4 | 4 | 4 | 12 | 12 | 12 | 4 | 4 |
| Palobayo | 1.5 | | 264 | 352 | | 13.3 | 26.7 | 53.3 | 53.3 | 2 | 4 | 4 | 4 | 12 | 12 | 12 | 4 | 4 |

## **Appendix B.** Data source for inventory analysis and LCIA.

**Table B1**

*Equipment specifications used to determine energy requirement*

| Equipment | Reference | Energy consumption |
|---|---|---|
| Oven | BINDER APT.line ED260 | 150.5 Wh/h |
| Grinder | AMBER MOE005002-CM157 | 160 Wh/h |
| Magnetic stirring and heating plate | Heidolph Instruments MR Hei-Standard | 558 Wh/h |
| Furnace | Vulcan 3-130 | 525 Wh/h |
| Oven | Lindeberg Blue M01420A | 250 Wh/h |
| Pressurized and heated cell for autohydrolysis | OFITE 170 | 500 Wh/h |

**Table B2**

*Life cycle inventory used in Simapro for LCIA of CPH co-product*

| Material or energy Input/output | Inputs | Outputs |
|---|---|---|
| Organic dry cocoa beans (kg) | | 117 |
| CPH co-product (kg) | | 1214 |
| Water, rain ($m^3$) | 77500 | |
| Supermagro (L) | 14 | |
| Lime, packed {RoW}\| market for lime, packed \| Cut-off, U (kg) | 146.7 | |
| Light fuel oil {CO}\| market for light fuel oil \| Cut-off, U (kg) | 44 | |
| Textile, jute {GLO}\| market for \| Cut-off, U (kg) | 1.1 | |
| Biowaste {RoW}\| treatment of biowaste, open dump \| Cut-off, U (kg) | | 332 |

**Table B3**

*Life cycle inventory used in Simapro for LCIA of activated carbon produced from CPH*

| **Material or energy Input/output** | **Inputs** | **Outputs** |
|---|---|---|
| Activated carbon (g) | | 1.55 |
| CPH co-product (g) | 42.8 | |
| Potassium hydroxide {GLO}\| market for \| Cut-off, U (g) | 3.3 | |
| Hydrochloric acid, without water, in 30% solution state {RoW}\| market for \| Cut-off, U (mL) | 4.2 | |
| Water, deionised {RoW}\| market for water, deionised \| Cut-off, U (mL) | 92.8 | |
| Venting of nitrogen, liquid {GLO}\| market for \| Cut-off, U (L) | 18 | |
| Energy, Electricity, medium voltage {CO}\| market for electricity, low voltage \| Cut-off, S (kWh) | | |
| *CPH drying (pre-treatment)* | 2.1 | |
| *CPH grinding (pre-treatment)* | 0.026 | |
| *Chemical activation* | 0.260 | |
| *Drying of CPH activated* | 1.375 | |
| *Pyrolysis* | 1.575 | |
| *Drying of activated carbon* | 1.0 | |
| Wastewater, average {RoW}\| treatment of, capacity 1E9l/year \| Cut-off, U (mL) | | 71.5 |

**Table B4**

*Life cycle inventory used in Simapro for LCIA of KOH produced from CPH*

| **Material or energy Input/output** | **Inputs** | **Outputs** |
|---|---|---|
| Potassium hydroxide (g) | | 1.3 |
| Calcium carbonate (g) | | 1.2 |
| CPH co-product (g) | 178 | |
| Water, deionised {RoW}\| market for water, deionised \| Cut-off, U (mL) | 51 | |
| Lime {RoW}\| market for lime \| Cut-off, U (g) | 0.54 | |

| | | |
|---|---|---|
| Energy, Electricity, medium voltage {CO}\| market for electricity, low voltage \| Cut-off, S (kWh) | | |
| *CPH drying (pre-treatment)* | 2.1 | |
| *CPH grinding (pre-treatment)* | 0.026 | |
| *Calcination* | 0.525 | |
| *Lixiviation* | 0.280 | |
| *Evaporation to obtain* $K_2CO_3$ | 0.280 | |
| *Caustification* | 0.140 | |
| *Evaporation to obtain KOH* | 0.280 | |
| Biowaste {RoW}\| treatment of biowaste, open dump \| Cut-off, U (g) | | 0.9 |

**Table B5**

*Life cycle inventory used in Simapro for LCIA of cellulose produced from CPH by alkali treatment*

| **Material or energy Input/output** | **Inputs** | **Outputs** |
|---|---|---|
| Cellulose (85% purity) (g) | | 3.2 |
| CPH co-product (g) | 71.2 | |
| Sodium hydroxide, without water, in 50% solution state {RoW}\| chlor-alkali electrolysis, diaphragm cell \| Cut-off, U (g) | 8 | |
| Water, deionised {RoW}\| market for water, deionised \| Cut-off, U (mL) | 398.6 | |
| Energy, Electricity, medium voltage {CO}\| market for electricity, low voltage \| Cut-off, S (kWh) | | |
| *CPH drying (pre-treatment)* | 2.1 | |
| *CPH grinding (pre-treatment)* | 0.026 | |
| *Alkali treatment* | 0.280 | |
| *Drying* | 1 | |
| Wastewater, average {RoW}\| treatment of, capacity 1E9l/year \| Cut-off, U (mL) | | 412.5 |

**Table B6**

*Life cycle inventory used in Simapro for LCIA of cellulose produced from CPH by autohydrolysis*

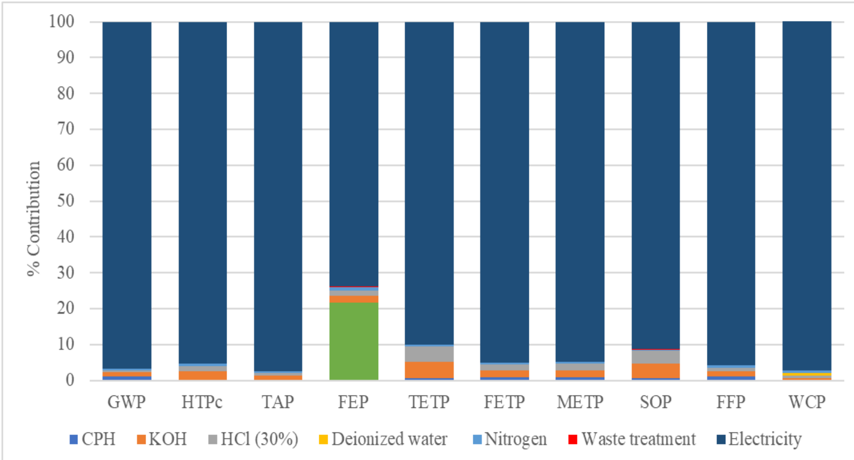
| **Material or energy Input/output** | **Inputs** | **Outputs** |
|---|---|---|
| Cellulose (63.5% purity) (g) | | 6.2 |
| CPH co-product (g) | 71.2 | |
| Water, deionised {RoW}\| market for water, deionised \| Cut-off, U (mL) | 130 | |
| Energy, Electricity, medium voltage {CO}\| market for electricity, low voltage \| Cut-off, S (kWh) | | |
| *CPH drying (pre-treatment)* | 2.1 | |
| *CPH grinding (pre-treatment)* | 0.026 | |
| *Autohydrolysis* | 0.1 | |
| *Drying* | 1 | |
| Wastewater, average {RoW}\| treatment of, capacity 1E9l/year \| Cut-off, U (mL) | | 100 |

**Appendix C.** LCIA result of CPH transformation into value-added products using solar energy for the CPH drying in the pre-treatment step instead of utilizing an oven.

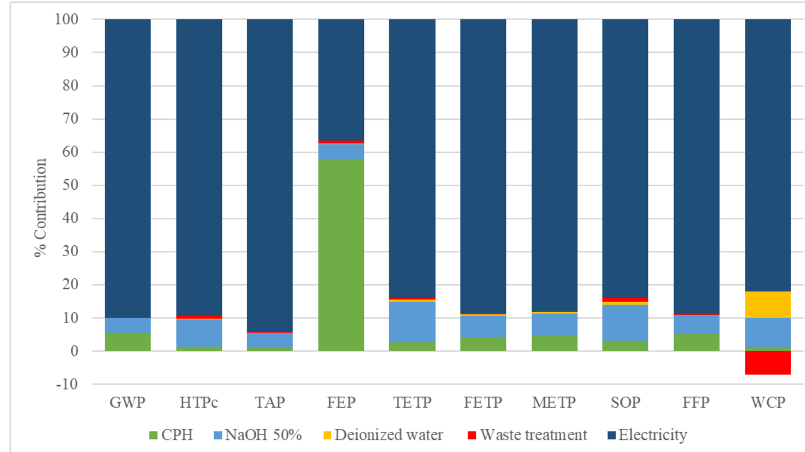
**Table C1**

Comparative life cycle impact assessment (characterization) using solar energy for the CPH drying in the pre-treatment step.

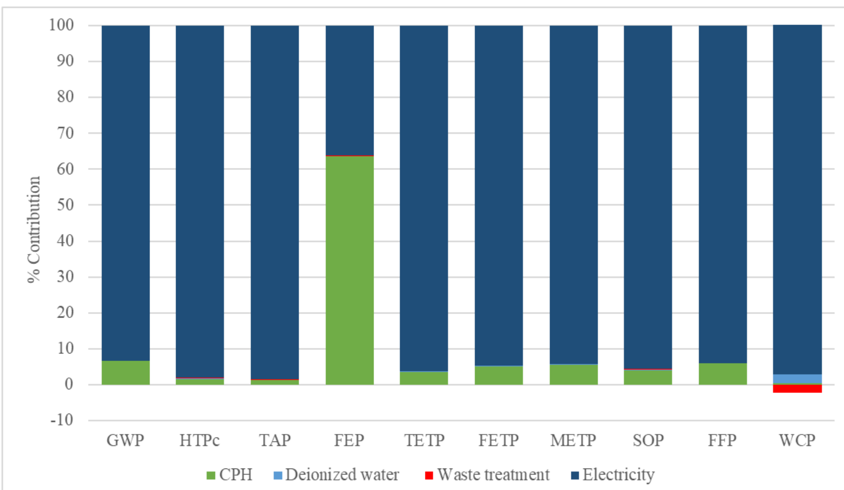
| Impact category (CFm) | Unit | AC | CAT | CAH | KOH | CPH disposal in open field |
|---|---|---|---|---|---|---|
| Normalized total score | | 0.118 | 0.025 | 0.020 | 0.006 | 0.011 |
| Global warming potential (GWP) | kg CO2 eq | 18.6626 | 3.7259 | 3.0681 | 0.8692 | 1.1577 |
| Human toxicity potential: cancer (HTPc) | kg 1,4-DCB | 0.5917 | 0.1173 | 0.0913 | 0.0246 | 0.0034 |
| Terrestrial acidification potential (TAP) | kg SO2 eq | 0.0720 | 0.0138 | 0.0113 | 0.0030 | 0.0003 |
| Freshwater eutrophication potential (FEP) | kg P eq | 0.0044 | 0.0016 | 0.0014 | 0.0006 | 0.0056 |
| Terrestrial ecotoxicity potential (TETP) | kg 1,4-DCB | 24.1952 | 4.8107 | 3.5943 | 0.9890 | 0.1799 |
| Freshwater ecotoxicity potential (FETP) | kg 1,4-DCB | 0.6238 | 0.1240 | 0.0993 | 0.0278 | 0.0257 |
| Marine ecotoxicity potential (METP) | kg 1,4-DCB | 0.7886 | 0,1574 | 0.1259 | 0.0354 | 0.0352 |
| Mineral resource scarcity (SOP) | kg Cu eq | 0.0214 | 0.0043 | 0.0032 | 0.0009 | 0.0002 |
| Fossil resource scarcity (FFP) | kg oil eq | 3.4200 | 0.6843 | 0.5540 | 0.1562 | 0.0454 |
| Water consumption (WCP) | m3 | 0.3600 | 0.0733 | 0.0562 | 0.0153 | 0.0009 |



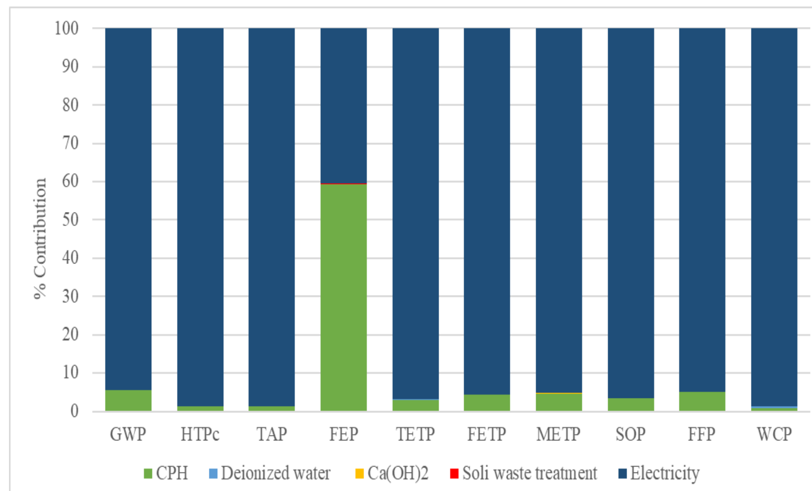

**D1a.**




**D1b.**




**D1c.**




**D1d.**

**Fig. D1.** Impact contribution by transformation processes to produce a. AC, b. CAT, c. CAH, d. KOH, using solar energy for the CPH drying in the pre-treatment step.