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**Production and use of biochar as soil  
conditioner with carbon offset credits and its  
Life Cycle Assessment**

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## Summary

In this thesis I investigate the role of pyrolysis as an efficient valorization process capable of producing biochar that could be employed as soil conditioner and eligible for carbon offset certification.

The first step of this work involved a comprehensive literature review to understand the complex mechanism of biomass pyrolysis for the production of biochar, biooil and gas, including the influence of the process parameters on the products and the equipment involved.

The second step focuses on the biochar application as soil amendment, investigating the advantages and disadvantages of its use, as well as the regulations associated with such implementation.

Then, the mechanisms of achieving Carbon Credits was analyzed, focusing on the Puro Earth Standard.

Finally, extensive experimental activity was conducted at the Institute for Chemical and Fuels from Alternative Resources (ICFAR) of Western University (Ontario, Canada). Cocoa shell, representing a significant residue of the chocolate manufacturing industry, have been processed in two different pyrolysis configurations: a lab scale horizontal mechanically fluidized bed operated in batch mode, and a larger scale horizontal mechanically fluidized bed operated in continuous mode, at temperature between 350°C and 650 °C.

The ultimate objective of this work was to perform a Life Cycle Assessment (LCA) related to the production and use of biochar as soil amendment with carbon offset credits. To ensure the consistency of the study, two scenarios were analyzed: an industrial-scale concept based on the continuous horizontal mechanically fluidized bed used in the experiment and an existing, commercially available, pyrolysis plant.

## Introduction & Research Objectives

The global climate crisis represents one of the most pressing challenges of our time, posing significant threats to ecosystems, economies, and human well-being worldwide. At the heart of this crisis lies the rapid increase in atmospheric greenhouse gas emissions, particularly carbon dioxide, which has led to unprecedented changes in Earth's climate systems.

A worldwide change in strategy related to the management of CO<sub>2</sub> is essential for mitigating climate change, protecting public health, preserving ecosystems and biodiversity, promoting sustainable development. This shift requires collaborative action at all levels of society, from individuals and communities to governments and businesses, to transition to a low-carbon, resilient, and sustainable future.

The management of waste and residues products represents a major opportunity in such a sense. The implementation of efficient valorization processes has several advantages, such as diverting waste away from landfills, reduce the demand of energy and virgin material, enhance the circular economy, with direct and indirect consequences on the greenhouse emissions.

The pyrolysis process is an important strategy for the management of waste products valorization. It consists of a thermal decomposition induced by heating the feedstock in an oxygen free ambient. This process is particularly effective when applied to products of low value, such as biomass residues, offering the possibility of obtaining high value products, such as biochar and chemicals.

Moreover, an added opportunity lies in the growing interest in marketing Carbon Credits that can be attributed to the sequestration of stable carbonized materials.

To assess the potential of slow pyrolysis process of biomass residues and its potential future application on industrial scale, a practical case study has been developed at the Institute for Chemical and Fuels from Alternative Resources (ICFAR) of Western University (London, Ontario, Canada) in partnership with a food processing company present in Ontario (CA). The biomass considered are cocoa shells, a residue produced by the food company. The commitment consists of a series of nine pyrolysis experiments: seven tests are performed with a lab scale horizontal mechanically fluidized bed unit operated in batch mode, with maximum temperatures ranging from 350°C to 650°C. This preliminary analysis aims at finding the optimal temperature to produce biochar, to maximize its quality (long term stability) and yield. Once the optimal condition has been identified, two tests were carried out in a larger scale horizontal mechanically fluidized pyrolysis reactor operated in continuous mode. This phase allowed us to assess the production of biochar on a larger scale.

The final goal of this work was to quantify the carbon credits generated through the production of biochar from cocoa shell and its application as soil amendment according to the Puro Earth standard. Moreover, to prove the consistency of the study, two case study have been considered: an industrial-scale concept based on the continuous horizontal mechanically fluidized bed used in the experiment and an existing, commercially available, pyrolysis plant.



# 1 CLIMATE CHANGE

The United Nations defines climate change as long-term global shifts in temperatures and weather patterns. Such shifts can be natural, due to changes in the sun's activity or large volcanic eruptions. However, since the 1800s, human activities linked to the burning of fossil fuels, changes in land use and deforestation have served as the primary drivers of climate change. (UNITED NATIONS, n.d.-b).

These activities are responsible for the production of greenhouse gases that accumulate in the atmosphere, creating a barrier that prevents the emission of the solar radiation reflected by the earth, trapping the radiation inside the atmosphere and, consequently causing the global warming.

The greenhouse effect is linked to gases like water vapor, carbon dioxide, methane, nitrous oxide, and ozone. Despite carbon dioxide relatively low global warming potential, significant attention is directed towards this gas due to its long persistence in the atmosphere, lasting thousands of years (US EPA, 2023).

To understand the magnitude of the phenomena, let's refer to the studies performed by NOAA and GML based on CO<sub>2</sub> concentration at Mauna Loa Observatory since 1958. Since then, the concentration of CO<sub>2</sub> in the atmosphere has consistently risen from 315ppm to approximately 420 ppm (+34%) as of 2023. Notably, over the last year, the rate of increase was about 2.48ppm/year, as illustrated in this Figure 1 (GML & NOAA, n.d.).

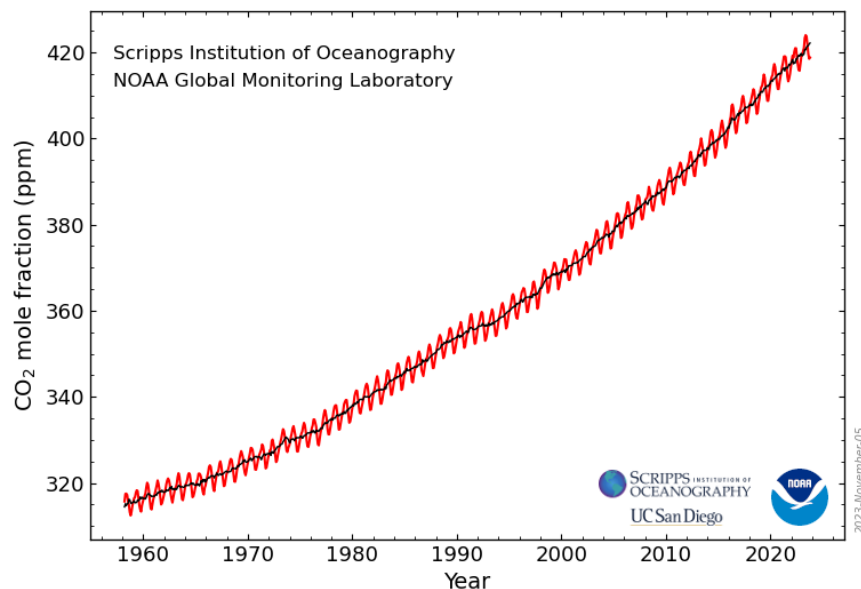


Figure 1: Atmospheric CO<sub>2</sub> at Mauna Loa Observatory (NOAA, s.d.)

The human-induced emissions concentrations allowed to reach an average global temperature increase of approximately 1°C above pre-industrial levels in 2017, with a rate of 0.2°C per decade. Indeed, the majority of land regions are undergoing more significant warming compared to the global average, whereas most ocean regions are experiencing a slower rate of warming. Depending on the temperature dataset considered, 20–40% of the global human population live in regions that, by the

decade 2006–2015, had already experienced warming of more than 1.5°C above pre-industrial in at least one season (IPCC, 2022).

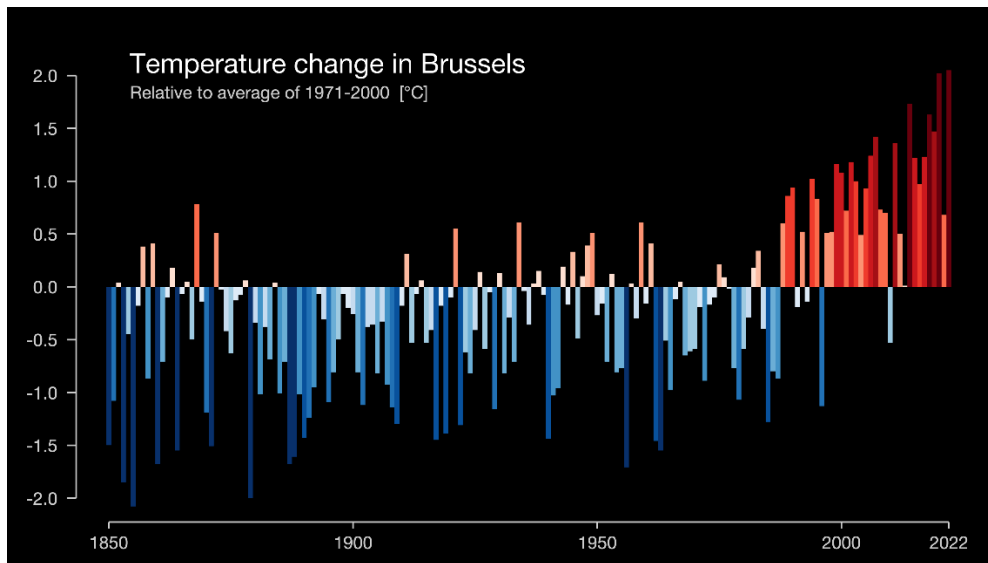


Figure 2: Yearly average temperatures change in Brussel relative to average of 1971-2000. The color of each stripe represents the temperature anomaly for a given year, or how much warmer (red) or colder (blue) that year was relative to the long-term reference period of 1981-2010 (University of Reading, n.d.).

As a consequence of these inhomogeneous temperatures increases, global climate is changing. Nowadays, the melting of the glacier surfaces is a well-known phenomenon, Antarctica is losing ice mass at an average rate of about 150 billion tons per year, and Greenland is losing about 270 billion tons per year (NASA, n.d.), adding to sea level rise.

The intensification of magnitude and frequency of extreme weather events has changed. According to Carbon Brief, of the 152 extreme heat events that have been assessed by scientists, 93% found that climate change made the event or trend more likely or more severe. For the 126 rainfall or flooding events studied, 56% found human activity had made the event more likely or more severe. For the 81 drought events studied, it's 68% (Pidcock & McSweeney, 2022).

These phenomena will be more and more frequent also in region of the world where it didn't happen before: in Italy, 41 extreme weather events occurred just in the first ten months of 2023, 4 per month. Over 114 extreme weather events recorded since 2010, 80 (70%) happened in the last 4 years (2020/2023) (ANSA, 2023).

This trend will result in the destruction of natural habitats, water shortages, desertification, and the eventual extinction of certain species, while also promoting the proliferation of viruses and bacteria, thus increasing the spread of more infectious diseases.

The occurrence of these impactful events highlights the necessity for a shift in course, directing policies and regulations not solely towards zeroing anthropogenic emissions but also towards decreasing the concentration of CO<sub>2</sub> in the atmosphere.

The Paris Agreement in 2015 defined the target: limit the increase of the global average temperature well-below 2°C above pre industrial levels, with efforts to limit that increase to 1.5°C above pre industrial levels (UNITED NATIONS, n.d.-a). However, in recent years, world leaders have stressed the need to limit global warming to 1.5°C by the end of this century.

The strategy to interrupt global warming foresees the achievement of Net Zero target, a condition in which the CO<sub>2</sub> emitted by anthropogenic activities are balanced by the amount of CO<sub>2</sub> subtracted.

In 2020 the European Green Deal has been approved, defining the strategies to reach the ambitious target of Net Zero by 2050. To assess such target is important to dedicate to both faces of the coins: on one side, abating carbon emissions, on the other, improving the removal of CO<sub>2</sub> from the atmosphere.

## 2 THEORETICAL FRAMEWORK

### 2.1 BIOENERGY

The bioenergy is a class of renewable energy related to the processing of biomass with the aim of producing heat, electricity, fuels and valuable chemicals products. Today, its implementation is constantly expanding within the context of reducing CO<sub>2</sub> emissions and seeking alternatives to fossil fuels.

Biomass is considered an intrinsically carbon-negative technology: the CO<sub>2</sub> emitted through the combustion of biomass is the same amount that is subtracted by the atmosphere by the process of photosynthesis during the plant growth. Instead, the burning of fossil fuels releases carbon that has been locked in the ground for millions of years displacing it in the atmosphere, increasing the overall concentration of CO<sub>2</sub>.

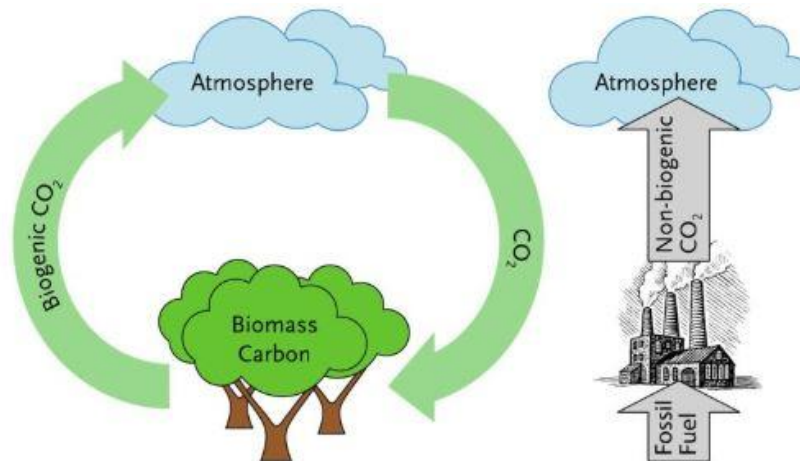


Figure 3 Fossil vs Biogenic CO<sub>2</sub> emissions (IEA, IEA Bioenergy, s.d.).

Moreover, the valorization of biomass residues avoids the natural biomass decomposition process that would result in the emission of pollutants such as methane and CO<sub>2</sub>. According to Scarlat et al., bioenergy continues to be the main source of renewable energy in the EU in terms of gross final consumption, counting for 116 Mtoe (59% of all renewables and 10% of all energy sources,) to the gross final energy consumption in 2016. In terms of end use, the largest sector is heating and cooling, which accounts for about 75% of all bioenergy consumed. Bioelectricity and transport biofuels account for 13% and 12% respectively (Scarlat et al., 2018).

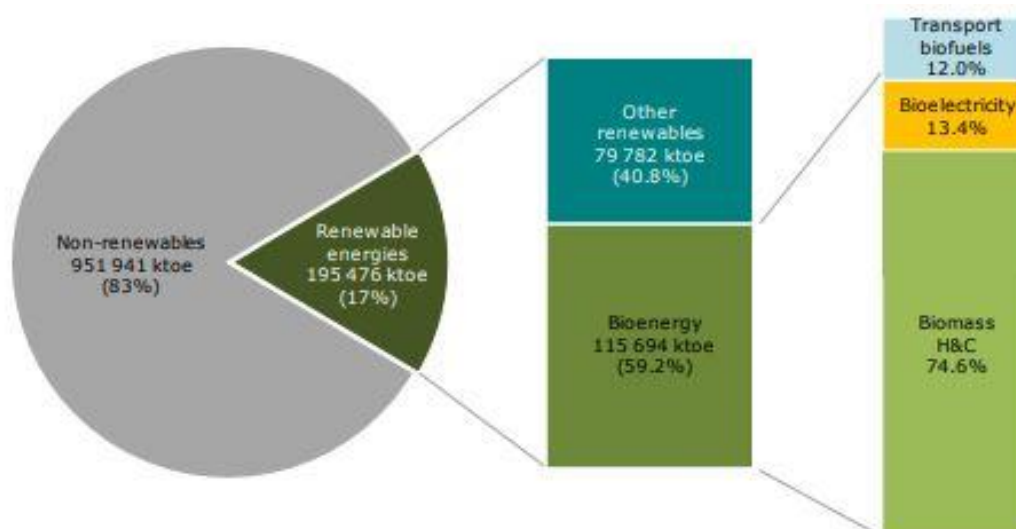


Figure 4 Share of renewables in the EU's gross final energy consumption for 2016 (Scarlat et al., 2018).

The deployment of bioenergy is already making a substantial contribution to meeting global energy demand. It has the potential to expand significantly in the future, offering greenhouse gas reductions and additional environmental advantages. It also aids in enhancing energy security, promoting social and economic growth in rural areas, and refining resources and waste and residues management.

In Figure 5 are summarized the main biomass conversion technologies.

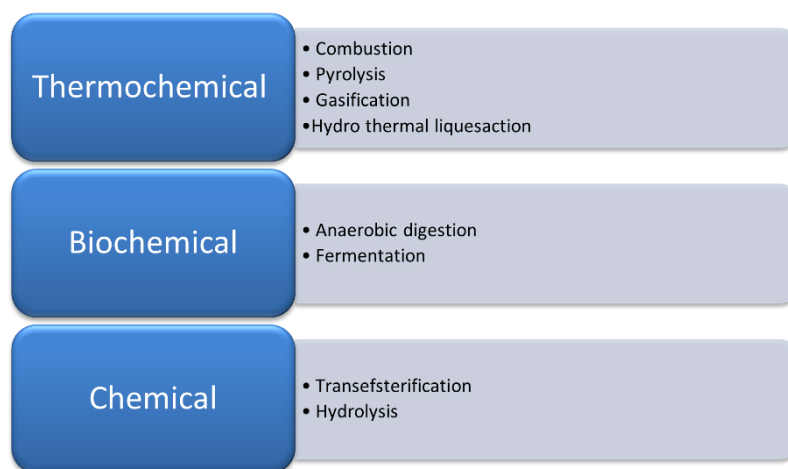


Figure 5 Classification of main biomass conversion technologies

## 2.2 BIOMASS

European Commission defines biomass as the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste (EU, 2009).

There are several ways to classify biomasses:

-based on the type of crops: woody (forest) or herbaceous (agricultural) crops;

- based on feedstock origin: dedicated (e.g. sugar cane, sunflower, sugar beet) or residual (straw, sawdust) and waste (e.g. used cooking oil, Organic Fraction of Municipal Solid Waste);
- based on the type of energy crops (ligno-cellulosic biomass, oleaginous, sugar/starch crops).

## 2.2.2 LIGNO-CELLULOSIC BIOMASS

The lignocellulosic biomass is derived from forestry residues and agriculture crop residues, available in abundance with no food or fodder value (N. Kumar & Dixit, 2021). Lignocellulosic biomass can be regarded as a complex heterogeneous mixture of three main structural organic components, namely cellulose, hemicellulose and lignin, associated with various organic and inorganic compounds (Vassilev et al., 2012). In detail, Cellulose ( $C_6H_{10}O_6$ ) is a condensed polymer of glucose ( $C_6H_{12}O_6$ ), linked together through  $\beta$ -1, 4-glycosidic linkages; it is the basic structural component of plant cell walls and it is the most abundant of all naturally occurring organic compounds (Britannica, 2023).

Hemicellulose is a polysaccharide composed of various sugar units such as xylose, arabinose, mannose, and galactose (N. Kumar & Dixit, 2021). With respect to cellulose, it features a much lower degree of polymerization of glucose units, on the other hand, the branched structure of hemicellulose is more complex than cellulose (N. Kumar & Dixit, 2021).

Lignin is a non-sugar organic polymer, mainly consists of three kinds of alcohol, i.e. p-coumaryl, coniferyl and sinapyl (N. Kumar & Dixit, 2021); provides structural support and rigidity to plant tissues and represents a barrier against microorganisms.

In general, lignocellulosic biomass has a typical composition of 40%– 80% cellulose, 15%–30% hemicellulose, and 10%– 25% lignin (Hakeem & Sharma, 2022).

Besides the three main constituents, lignocellulosic biomass also contains water, extractives and ashes. Extractives in biomass refers to non-structural components<sup>1</sup> that can be extracted by solvents (e.g. water, ethanol, benzene). They add properties color, taste, odor and decay resistance to biomass. They comprise tannin, volatile oils, fats, waxes and gums.

Ashes are constituted by the inorganic compounds present in the biomass. The ash content in biomass is derived from two primary sources: introduced ash collected during harvest and processing, and biogenic ash inside of the plant tissues due to normal biological processes (Lacey et al., 2018).

## 2.3 BIOMASS THERMOCHEMICAL CONVERSION TECHNOLOGIES

Thermochemical processes use heat to induce chemical transformation of biomass resulting in energy and valuable products such as liquid fuels (bio-oil), solid (biochar) and chemicals.

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<sup>1</sup> Non-structural components: Non-chemically bound components of biomass that include but are not limited to sucrose, nitrate/nitrites, protein, ash, chlorophyll, and waxes (Sluiter et al., 2008).

The first thermochemical process is certainly the combustion of biomass. It consists in the complete oxidation of the solid feedstock producing useful for several purposes (heating, cooking, electricity and power production). The process of biomass combustion is characterized by a series of phases (thermochemical processes) that can be more or less distinct:

- 1- *Drying*: the heat penetrates the biomass causing the evaporation of the water content ( $T < 100^{\circ}\text{C}$ ). The evaporation absorbs energy released during the combustion process, causing a reduction of the temperature in the combustion chamber. For this reason, the moisture content is a very important fuel variable.
- 2- *Pyrolysis*: locally occurs a thermal degradation (devolatilization) in absence of an externally supplied oxidizing agent. The main products of this process are Tars<sup>2</sup> in vapor phase, solid carbonaceous charcoal and low molecular weight incondensable gasses ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ).
- 3- *Gasification*: locally occurs a thermal degradation (devolatilization) in presence of an externally supplied oxidizing agent at a temperature between 800 and  $1100^{\circ}\text{C}$ . In this process the gas product is the main yield ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{CH}_4$  and other hydrocarbons).
- 4- *Char oxidation and Gas phase oxidation*.

It is worth noticing that each phase of the combustion process constitutes a thermochemical process by itself and, depending on the conversion technology adopted, the type of biomass and the design of the process parameters, it is possible to define the relative importance of the phases, obtaining the desired process.

Torrefaction is substantially a pyrolysis at low temperature ( $200\text{--}300^{\circ}\text{C}$ ) aiming at increasing the energy content of biomass; the feedstock is heated up to in an oxygen depleted environment for rather long time (5 minutes to some hours), in this period the solid feedstock partially devolatilizes (drying of water, volatiles gasification) but the initial energy content is mainly preserved in the solid product, resulting in the production of low molecular weight gasses and condensable vapors (Wild & Calderón, 2021) (Shankar Tumuluru Shahab Sokhansanj Christopher Wright J Richard Hess Richard D Boardman et al., 2011)

### 2.3.2 PYROLYSIS

Pyrolysis is a thermochemical process for feedstock conversion into a large range of possible value-added products, like fuels and chemicals obtained from bio-oil processing and solid biochar. The process is performed in an oxygen-free ambient (limited presence) where the solid biomass is decomposed using heat. Three products always result from this process: a solid carbonaceous material (biochar), a mixture of condensable vapors (once recovered as liquid it originates the pyrolysis oil) and a mixture of permanent (incondensable) gases; the proportions can be varied over a wide range by adjustments of the process parameters and depending on the feedstock properties. During the last decades pyrolysis has been widely investigated as valorization technology to improve circular economy, striving for a zero-waste target.

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<sup>2</sup> IEA Gasification Task meeting (Brussels, March 1998) refer to Tars as “all organics boiling at temperatures above that of benzene ( $\sim 80^{\circ}\text{C}$ ) should be considered as ‘tar.’” (Milne & Evans, 1998).

The pyrolysis process can be classified as described in Table 1:

Table 1: Classification of pyrolysis processes with respect to the operating parameters (Kazawadi et al., 2021; Leng & Huang, 2018; Montoya et al., 2015; Pecha & Garcia-Perez, 2020)

Mode	Conditions	Yield (wt %)		
		Liquid	Char	Gas
<b>Slow (Carbonization)</b>	<ul style="list-style-type: none"> <li>• Temperature: 350-650°C</li> <li>• HR: &lt;10°C min<sup>-1</sup></li> <li>• RT: very long (minutes to days)</li> <li>• HVRT: long, 5-30 minutes</li> <li>• Particle size: large, &gt;2mm</li> </ul>	30-50%	25-35%	~30%
<b>Intermediate</b>	<ul style="list-style-type: none"> <li>• Temperature: ~500°C</li> <li>• HR: 1-10°C s<sup>-1</sup></li> <li>• RT: moderate (minutes to hours)</li> <li>• HVRT: short, 10-30 s</li> <li>• Particle size: moderate, 1-5 mm</li> </ul>	35-50%	25-30%	20-30%
<b>Fast/Flash</b>	<ul style="list-style-type: none"> <li>• Temperature: 400-650°C</li> <li>• HR: &gt;16 °C s<sup>-1</sup> (fast)</li> <li>• HR &gt; 100°C s<sup>-1</sup> (flash)</li> <li>• RT: very short, 0.5-10 s</li> <li>• HVRT: very short, &lt;2 s</li> <li>• Particle size: small, &lt;2mm</li> </ul>	60-75%	15-25%	10-20%

*Slow pyrolysis* is meant for the production of solid char having vapors and gases substantially as byproducts, often combusted to recover process heat and/or electricity. There is no interest in fast removal of vapors, that continue to react with each other, as the solid char and any liquid are being formed. Long solid residence times allow the production of charcoal considering the low heating rate and the feedstock dimensions (poor heat transfer inside the material) and moisture.

On the other hand, the target of *fast pyrolysis* is the maximization of the liquid yield. For this purpose, the hot vapors are immediately removed to avoid secondary cracking reactions of the tars that causes the braking of molecules into smaller ones that go into gas phase, reducing the liquid yield. Moreover, very small particles size and very high heating rate allows to increase the kinetic of the reaction, reducing the residence time of the solid char that act as catalyst for secondary cracking of vapors.

*Intermediate pyrolysis* has intermediate targets, trying to maximize both the liquid and solid phase. Considering the smaller particle size and higher heating rate, the solid residence time is shorter than in slow pyrolysis but still considerable long with respect to fast pyrolysis and a short hot vapor residence time allows the maximization also of the liquid phase.



Biomass pyrolysis is a very complex system, involving simultaneous solid heat transfer, solid-phase chemical reactions, liquid evaporation and thermal ejection, liquid phase reactions, mass transfer of vapors through the solid matrix, and vapor-phase reactions (Pecha & Garcia-Perez, 2020). According to Mohan et. al., the general pyrolysis process can be described by the following steps (Mohan et al., 2006a):

1. Heat transfer from a heat source, to increase the temperature inside the fuel and drying of water content (100°C);
2. The initiation of primary pyrolysis reactions at this higher temperature releases volatiles and forms char
3. The flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler non-pyrolyzed fuel;
4. Condensation of some of the volatiles in the cooler parts of the fuel, followed by secondary reactions, can produce tar;
5. Autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions (item 2, above) simultaneously occur in competition; and
6. Further thermal decomposition, reforming, water gas shift reactions, radicals recombination, and dehydrations can also occur, which are a function of the process's residence time/temperature/pressure profile.

Pyrolysis reactions can be classified into primary and secondary reactions. Primary reactions occur on cell walls and refer to the decomposition of the three main constituents of lignocellulosic biomass (i.e. cellulose, hemicellulose and lignin) leading to the formation of primary products (e.g. levoglucosan) and intermediate. When primary products and intermediates are exposed to the effects of heat and natural catalyst, secondary decomposition and volatilization reactions arise (Pecha & Garcia-Perez, 2020). Hemicellulose and cellulose are the major composition of the volatile matter, while lignin constitute the main composition for char formation (Adjin-Tetteh et al., 2018).

To have a better understanding of the thermal decomposition behavior of cocoa shells during pyrolysis, let's refer to the TGAs and DTGAs performed by Mumbach et al. and Najafabadi et al. represented in Table 2:

Table 2 TGA of Cocoa Shell and Cocoa Shell powder.

Biomass	Cocoa shell	Cocoa shell powder
Heating rate	5-10-20-30 °C/min	10 °C/min
Moisture evaporation	37-151 °C	<180°C
Extractives devolatilization	127-251 °C	
Hemicellulose devolatilization	209-306 °C	180-280°C
Cellulose devolatilization	297-327 °C	280-350°C
Lignin Decomposition	346-627 °C	350-650°C

### 2.3.2.2 REACTORS DESIGN

The pyrolysis reactor design is a very wide research topic. Depending on the required products targets several designs had been proposed in last decades, starting from the very low tech Brazilian “hot-tail” kilns for carbonization to the more advanced circulating fluidized bed for fast pyrolysis. A brief description of the main reactors employed in slow/intermediate pyrolysis (i.e. converters) is provided in the following section.

#### 2.3.2.2.2 Batch reactors

The batch reactors are closed systems, feedstock feeding is discontinuous. It is loaded before the experiment and can be discharged only when the reaction is finished. These types of reactors find primary use in laboratory testing. The simple design makes them cost-effective, flexible, and easy to operate, particularly with minimal feedstock. Maintenance is also simplified, and overall, the batch process demonstrates good scalability. Main drawbacks of this configuration are the high labor cost and the composition of the resulting product that may vary from one batch to another. Pyrolysis reactions are most likely performed in semi-batch reactors, an intermediate solution allows the introduction of further reactants while the reaction is occurring. Usually, an inert gas stream is introduced to obtain an oxygen depleted ambient and promote gaseous products removal, improving also the control on reaction exothermicity.

In a thermochemical process as pyrolysis, the heat transfer is a key point, the possibility of using a stirrer allows a better mixing of the bed material, enhancing the heat transfer, reducing the fraction of unreacted material, resulting into a more uniform temperature distribution inside the bed.

#### 2.3.2.2.3 Continuous reactors

Continuous reactors are open systems, the feedstock supply and the products removal are continuously performed while the reactor is operated. The design of the feeding system represents a challenge for this configuration, considering the difficulty of handling the transport of feedstock inside the reactor without introducing undesired atmospheric oxygen. These reactors can handle chips and pellets as well as crushed or chopped material such as sugar cane bagasse, bark, twiglets, olive stones, and coconut shells (Garcia-Nunez et al., 2017). Continuous reactors feature high production capacity and stable product composition, a higher degree of automation allows reduced labor cost. On the contrary, are less flexible than batch reactors as they are designed for specific feedstock. Furthermore, the initial investment required is considerably high, large-scale plants with large processing capacity represent a more cost-effective solution. The heat is generally supplied indirectly by means of external burners or electric heaters, more efficient solutions exploit the heat from the combustion of the gaseous yield (e.g. gaseous, gaseous and vapors) to sustain the process.

The following lines contain a description of the main pyrolysis reactors operated in continuous mode:

### Rotary Kiln

Rotary kilns are the preferred reactor configuration for the thermal treatment of particulate solids and considerable research has been undertaken to study their behavior for the treatment of biomass (Babler et al., 2017). It consists of an internal concentric steel tube and a cylindrical internally insulated mantle that makes up the rotary part. The residence time of the feedstock inside the reactor is defined by the inclination angle of the drum and the rotation speed (Bongo Njeng et al., 2015). The heat can be supplied directly or indirectly, usually is gathered burning gasses and pyrolysis vapors (Babler et al., 2017). Advantages of these reactors are flexibility in term of shape and size, the scalability, the extensive mixing in the reactor, and the absence of moving parts in the interior (Pichler et al., 2021).

Table 3: Possible of Operating Parameters for Rotary kiln reactor for intermediate pyrolysis of Cocoa shell

Biomass	Pyrolysis mode	Feeding Rate	Temperature	Heating Rate	Residence Time	HVRT	Ref.
Ground cocoa pod husks	intermediate	110g/h	550-600°C	400°C/min	3,2 min	2-4 min	(Adjin-Tetteh et al., 2018)

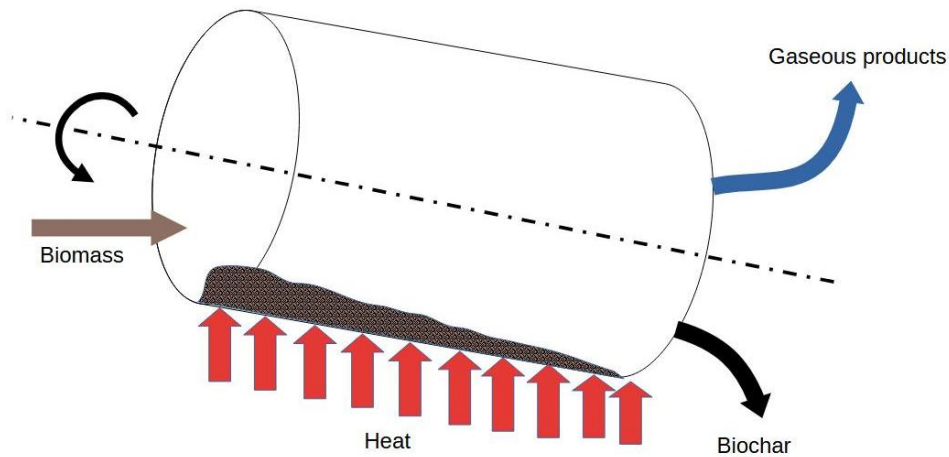


Figure 6: Schematic representation of Rotary Kiln pyrolysis reactor



Figure 7: Rotating kiln carbonization pilot plant, capacity 100 kg/h of biomass (ReCord, n.d.).

### *Auger reactor*

The auger reactor is an attractive solution due to its versatility in transforming a wide range of feedstocks, relatively simple construction and low energy requirements (Raza et al., 2021). The concept is based on the helical screw mechanism used to carry the biomass particles through the reaction vessel. The feeding is typically performed through a hopper and/or a feeding screw. The residence time is defined by the type of screw employed for moving the bed and its rotation speed (Mathew & Muruganandam, 2017). These reactors can be operated with or without heat carriers (Brassard et al., 2017).

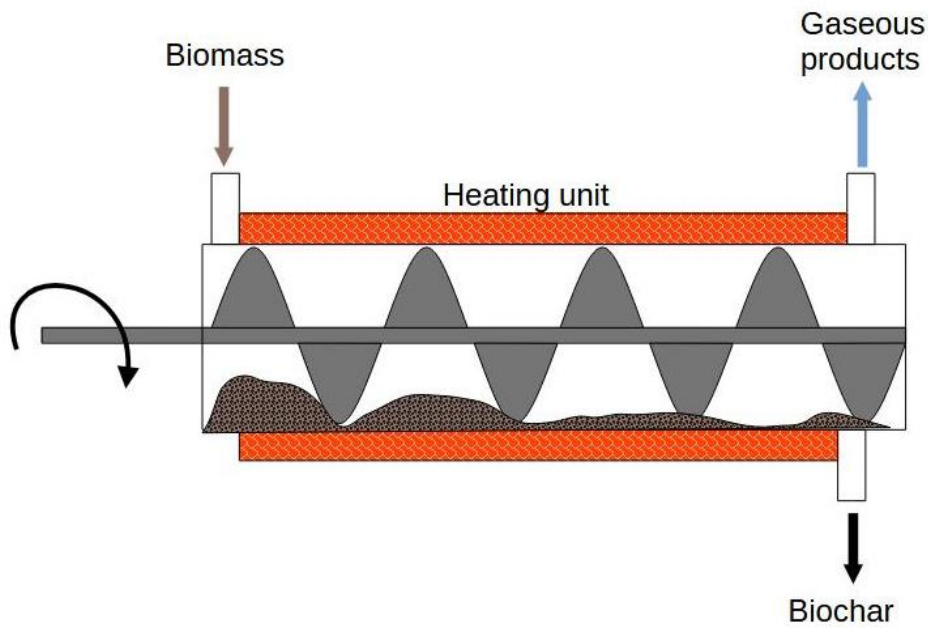


Figure 8: Schematic representation of the Auger reactor

Another design based on a conveyor mechanism inside the reactor is the moving agitated bed reactor, in which biomass is transported by patented mixers over a horizontal surface heated by molten salts (Garcia-Nunez et al., 2017).

#### *Paddle pyrolysis reactor*

Another possible configuration has been created with the purpose of having a simple design that allows good mixing of the biomass bed, enhancing the heat transfer. This horizontal reactor exploits an internal stirring mechanism to move and mix the feedstock (Garcia-Nunez et al., 2017). It worth to also mention its flexibility in managing different types of feedstocks and the low price.

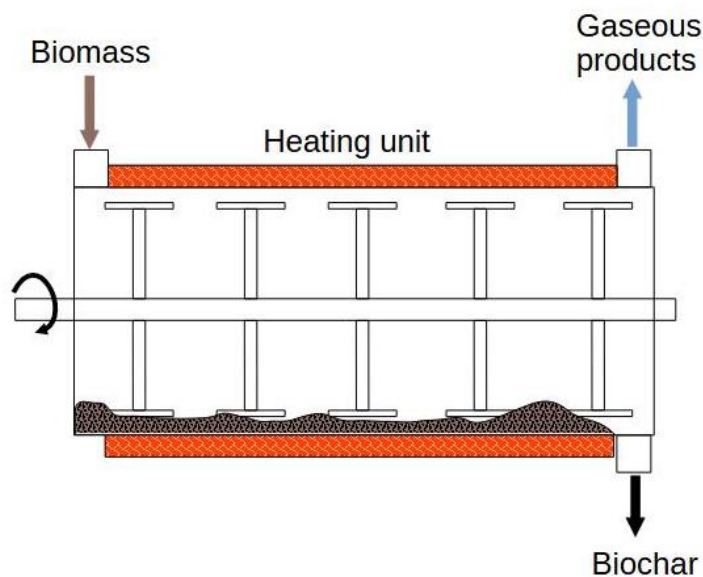


Figure 9 Schematic representation of a Paddle reactor

### 2.3.2.3 PROCESS PARAMETERS

In detail, the parameters that govern the pyrolysis reaction are investigated:

- *Process temperature and heating rate:* A rapid heating and cooling of primary vapors are necessary to minimize the extent of secondary reactions that reduce the liquid yield and have a negative impact on its quality; instead, slow heating values lead to higher char yields (A. Sharma et al., 2015). It is worth to notice that there is no point in adopting drastic heating rates because mass and heat transfer mechanisms will limit the process (Kan et al., 2016a). Research from Zhao et al. demonstrates the presence of an optimum heating rate for char maximization, above that value the enhancement of organic breakdown and release of carbon-rich vapors reduce the solid yield (Zhao et al., 2018).

Temperature has a significant impact on pyrolysis yields and properties. Referring to solids, higher temperatures lead to lower char yields with an increase of the carbon content, as demonstrated in the studies of (Demirbas, 2007a) and (Xiao & Yang, 2013). On the other hand, low temperatures may lead to incomplete decomposition of the bed, resulting in unpyrolyzed biomass in solid char. To assess the effects of temperature on liquid yield, let's refer to work done by Demirbas on different biomasses; it reveals that the liquid yield is a function of the temperature, particularly, for all the samples analyzed, peak in oil production is reached in the range of temperature 450-550 °C (Demirbas, 2007b). Above the peak of the liquid yield, secondary decomposition reactions become more dominant, resulting in an increase of the gaseous yield (Garcia-Perez et al., 2008). The increase in temperature leads to a monotonous increase in the heating value of organics in dry basis, nevertheless, the HHV of the liquid phase (wet base) decreases after the peak temperature for liquid production is reached (Garcia-Perez et al., 2008) due to the increase of the water content produced by secondary decompositions. Elevated temperature can produce high quality non-condensable gas with high HHV which can be used as a source of energy (He et al., 2018).

- *Pressure*: Basile et al. study on the heat of biomass pyrolysis reveals that an increase of the operating pressure results in a lower heat demand and in an increase in the final char yield, suggesting the presence of a competitive mechanism between the endothermic primary decomposition process and the exothermic vapor–solid interactions. The outcome highlights that an increase in the operating pressure reduces the heat requirements of the pyrolysis process, and the heat of pyrolysis reactions may shift from endothermic to exothermic (Basile et al., 2014). According to Manyà et al., increasing the pressure (keeping constant residence time) has a negative effect on biochar yield but a positive effect on char carbon composition. Moreover, pressure has a positive effect on the pyrolysis gas production at the expense of the liquid fraction. The fraction of methane in the producer gas significantly increases with pressure due to the promotion of the methanation reactions (Manyà et al., 2014).
- *Solid residence time (RT)*: increasing the total residence time enhances gas yield and reduces solid and liquid yields, though the solid yield is not very much affected by the increase of the residence time, while the effect on the liquids is much stronger (Zhao et al., 2018).
- *Hot vapors residence time (HVRT)*: short vapor residence time reduces the occurrence of secondary decomposition reaction of pyrolysis vapor, increasing the liquid yield (Bridgwater et al., n.d.). Qureshi et al. agree with the mentioned trend revealing also that increase the residence time has effect on liquid yield quality, observing a decrease in carbon content and an increase in oxygen content, this indicate that biooil produced at longer vapor residence time has poorer stability due to its high oxygen level (Qureshi et al., 2021).
- *Biomass particle size*: The useful particle size depends on the pyrolysis mode adopted, the type of reactor and the kind of biomass itself. In fast pyrolysis, for example, high heat and mass transfer must be guaranteed for the correct execution of the process, these mechanisms are enhanced by adopting small feedstock particles. The study proposed by Bennadji et al. showed that centimeter scale biomass size manifest a behavior typical of thermally thick biomass pyrolysis, with significant intraparticle temperature gradients and an evident impact of reaction thermochemistry on the temperature fields. The main impact of particle size was on the timing of the heating and devolatilization processes, both increasing with the size (Bennadji et al., 2014). This likely gives rise to an increase in char yields and a decrease in the bio-oil and gas product yields (Yorgun & Yildiz, 2015). The effect of particle size is explained in terms of heating rate: bigger particles heat up slower causing lower temperature of average particles, resulting in less volatile production (Aysu & Küçük, 2014). Moreover, increasing the particle size led to increase of water content of pyrolysis liquid (Garcia-Perez et al., 2008) and decrease carbon content of solid char. On the other hand, smaller particles improve the heat transfer, higher heating rate is possible under equal process conditions. At the same time, smaller particle size required higher pretreatment cost.
- *Biomass initial moisture*: the lowest possible water contents in biomass are advisable for pyrolysis purposes, evaporation of water requires a large amount of heat, affecting the process efficiency; it is also notable that completely dried biomass feedstock suffers heat transfer

limitations because of its low heat conductivity (Akhtar & Saidina Amin, 2012). A minimum amount of initial moisture (below 10% (Guedes et al., 2018)) is necessary because water acts as a reactant for biomass species and as heat transfer medium, which enhances pyrolysis (Demirbas, 2004). Moreover, a certain level of initial moisture is beneficial to the oil yield because provides stabilization of thermal decomposition fragments (pyrolysis products) and dissolution of water-soluble fragments (Akhtar & Saidina Amin, 2012). On the other hand, an excess of water lowers the lower heating value (LHV) of the pyrolysis oil and affects its chemical stability and quality (Guedes et al., 2018) (e.g. among others, can lead to phase separation).

- *Sweeping gas*: the purpose of the carrier gas is to purge the pyrolysis reactor from pyrolysis vapors avoiding secondary reactions and to ensure an oxygen-free ambient. Commonly used gases are N<sub>2</sub> and Ar. Recent study from Premchand et al. highlight the potential of using CO<sub>2</sub> in slow pyrolysis, resulting in an increase in biochar yield and its characteristics (surface area and porosity, nutrients and mineral contents, carbon and ash contents, aromaticity, stability and abiotic aging) (Premchand et al., 2023).. Changing the sweep-gas flow rate affects the yields; in particular, poor vapor extraction enhances the gas production to the detriment of the liquid yield, at same time, gas speed might affect the condensation of vapors inside the condensers, impacting on the liquid yield and its properties (Kim et al., 2016). Regarding the effect of carrier gas on biochar production, it has been proven by many researchers that increasing heat carrier flow rate has negligible effect on the biochar yield, as noticed by Tripathi et al. in their review study (Tripathi et al., 2016).
- *Catalyst*: Catalytic pyrolysis is performed in two ways, either by mixing biomass and catalyst (in-situ), where the catalyst plays an important role in carrying the heat, or in a dual-bed reactor, where biomass and catalyst beds are separated (ex-situ). The first method requires a lower capital investment as is only requires a single reactor. However, catalyst deactivation from char formation occurs more quickly. Moreover, poor contact between the two solid surfaces (biomass and catalyst bed) leads to poor heat transfer. The ex-situ mode is highly selective to desirable aromatics because this configuration allows individual control of both the pyrolyzer and the upgrading reactor's operating conditions. However, this configuration is more complex and leads to a higher capital cost (Norouzi et al., 2021). There are several ways in which catalyst modify the pyrolysis process (A. Sharma et al., 2015):
  - 1- Decrease of the decomposition temperature of biomass.
  - 2- Catalysts affect the network of reaction, i.e., deoxygenation which allows in situ upgrading of bio-oil by reducing oxygenated organic compounds. The presence of catalyst also reduces polymerization precursors for stabilizing bio-oil.
  - 3- Decarboxylation, decarbonization and dehydration reactions may release more CO, CO<sub>2</sub>, and H<sub>2</sub>O when catalysts are employed.
  - 4- Catalysts promote the formation of char due to dehydration reaction.

Slow pyrolysis of biomass generally does not make use of additional catalyst, the char itself acts as a catalyst for secondary cracking reactions. The use of catalyst is oriented at improving the quality of bio-oil, main materials involved are zeolites, nickel, iron, cobalt.



- *Biomass pretreatments*: improve the processability of feedstock enhancing the overall pyrolysis process efficiency. Generally, these processes aim at reducing the particle size and decrease the moisture content. Commonly used processes are grinding and densification; in the first case, as the name suggests, the goal is the reduction of the particle size, this has a beneficial effect on process. Densification process aim at increasing the feedstock density, reducing the feedstock into small pellets; this process also favors the loss of a fraction of the initial moisture content. The reduction of size of particles and the increase of density is beneficial also for the transport and storage of the biomass, facilitating also the feeding inside the pyrolysis reactor; nevertheless, it is worth to underline that these processes are energy intensive affecting in the cost of the overall valorization process. Moreover, there is the possibility of thermal processing the feedstock through torrefaction process (described at the beginning of thermal decomposition processes) at temperature between 200-300°C; the main advantage of this operation is the energy densification, in fact, thanks to a partial thermal decomposition, the biomass loses its moisture and a fraction of volatiles components, without significantly affect its energy content; moreover, it improves hydrophobicity and grindability of the biomass (Nhuchhen et al., 2014). Another biomass pretreatment process commonly used is the steam explosion. It consists of an explosive decompression that results in the degradation of mainly hemicellulose and lignin component of biomass causing large pores in biomass and improving the accessibility to cellulose component (R. Kumar et al., 2020), the process requires a considerable amount of energy to produce steam and to further dry the output material before pyrolysis. For sake of completeness, it is worth mentioning the existence of chemical pretreatment methods, such as acid and alkali pretreatment, hydrothermal pretreatment and ammonia fiber expansion. These techniques aim destroying the lignocellulosic structure, decrease the thermal stability and alter the components in the biomass (Kumar et al., 2020).

#### 2.3.2.4 PYROLYSIS PRODUCTS

The first remarkable consideration about pyrolysis yield is that three products (i.e. solid, liquid and gas) are always present, regardless of all process specifications. Instead, their relative quantities and quality are function of the process parameters.

##### *Solid*

The solid fraction of biomass pyrolysis is represented by the biochar, a low density, porous carbonaceous material obtained from the decomposition of mainly lignin and cellulose (Ranzi et al., 2017). It is made up of two main structural fractions: stacked crystalline graphene sheets and randomly ordered amorphous aromatic structures. Within the aromatic structures are incorporated other heteroatoms, such as hydrogen, oxygen, nitrogen, phosphorus and sulfur, contributing to the high heterogeneous chemistry and reactivity of biochar (Verheijen et al., 2010). The elemental composition is represented by C, H, N, S, O weight fractions that can significantly vary according to the biomass selected and the process parameters involved; the study done by Tsai et al. on biochar from cocoa pod husks pyrolysis reveals the following elemental compositions Table 4.

Table 4 Cocoa Pod Husks biochar elemental analysis (Tsai et al., 2018)

Ultimate analysis (wt% DB)	Temp.(°C)	Residence time (min)	C	H	N	S	O	O/C	H/C
CPHBC <sup>3</sup>	310	30	53,6	3,9	2,7	0,6	39,4	0,6	0,9
CPHBC	340	30	60,1	4,0	2,8	0,3	32,8	0,4	0,8
CPHBC	370	30	62,3	3,8	2,4	0,3	31,2	0,4	0,7
CPHBC	370	60	60,2	3,1	2,4	0,4	33,9	0,4	0,6
CPHBC	370	90	59,8	2,9	2,3	0,4	34,6	0,4	0,6
CPHBC	370	120	53,2	2,7	2,0	0,6	41,2	0,6	0,6

It is evident the dependance of carbon content on the pyrolysis temperature and on the residence time. Regarding proximate analysis, biochar is mainly constituted by fixed carbon, volatiles, ashes and moisture. Currently no data related to cocoa shell biochar proximate analysis are available, let's refer to more general data related to biochar composition of a variety of source materials and pyrolysis conditions: fixed carbon can generally range from 50 to 90% (wt%), volatile matter between 5% to 40% (wt%) the ashes around 0,5 to 5% (wt%) (for good quality charcoal) and the moisture content can range between 1 to 15% (wt%) (Jafri et al., 2018). The higher heating value of cocoa pod husk biochar varies in the range 18-25 MJ/kg, slightly lower than the one of fossil coal (Tsai et al., 2018). It is important to highlight that the high level of carbon and the aromatic structure of biochar are constants regardless of the biomass involved and pyrolysis modalities (Verheijen et al., 2010). The field of application of the biochar is very wide; thanks to its chemical-physical characteristics, the use of biochar in agricultural soils has attracted a lot of interest in the recent past. Introducing biochar or its composites into soil has the potential to alter numerous soil properties, including physical and chemical composition, microbial activity, soil fertility, and pollution levels. The magnitude of these effects is closely intertwined with the specific characteristics of the biochar employed (Premchand et al., 2023). Moreover, the use of biochar into the soil represents a very interesting option as carbon sequestration mean(Li & Tasnady, 2023), due the high concentration and recalcitrance of the carbon, contributing to the reduction of the content of CO<sub>2</sub> in the atmosphere. Other relevant applications of the biochar are waste water and remediation of contaminated soils through adsorption mechanism enhanced by biochar surface area, porosity and presence of functional groups (Ji et al., 2022). Moreover, biochar can be used for metallurgical applications (Ye et al., 2019), catalyst (Lee et al., 2017), gas purification (Bamdad et al., 2018) and construction material (Zhang et al., 2022) and combusted to provide energy to the pyrolysis process.

### Liquid

<sup>3</sup> Cocoa pod husk biochar

The condensed fraction of slow/intermediate pyrolysis vapors is a strongly heterogeneous liquid constituted by two phases: an aqueous phase (between 15-35% of the liquid yield), rich of oxygenated organic compounds of low molecular weight (e.g. acetic acid, methanol, acetone, ...), and an oily phase containing high molecular weight organic compounds, the bio-oil (Demirbas, 2007b). The presence of water represents an obstacle, enhancing the possibility of having phase separation and strongly decreasing the energy density of the liquid. Bio-oil is characterized by high viscosity, poor higher heating value (16-25 MJ/kg (M. Sharma et al., 2019)(Mohan et al., 2006a)), poor stability, and high corrosivity due to the presence of oxygenated compounds. The possible application of bio-oil is very wide:

- Fuel production: bio-oil can be upgraded to remove oxygen with minimal hydrogen consumption, while retaining the carbon content (T. Yang et al., 2019);
- Chemical precursor: biooil contains a large quantity of chemical compounds of interest, as acetic acid, acetone, butanol, economically more attractive than fuel production (Pinheiro Pires et al., 2019)
- Heat and power generation: bio-oil and in general pyrolysis vapors can be used as fuel for heat supply to the pyrolysis process, moreover Bio-oil can be burned directly for heat and power generation in boilers, furnaces, and gas turbines, contributing to renewable energy production.

### *Gas*

The gas fraction of lignocellulosic biomass pyrolysis is represented by the incondensable fraction of the vapors formed during primary decomposition and secondary cracking reactions. The gas mixture is mainly constituted by carbon dioxide, carbon monoxide, methane, oxygen, hydrogen and nitrogen (Y. Yang et al., 2014), while might be traces of small chain hydrocarbons (e.g. C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>), nitrogen oxide and sulfur oxides; the relative compositions change according to a large number of parameters, such as biomass composition, process temperature and hot vapor residence times. According to the products distribution, the LHV can range between 10 and 20 MJ/Nm<sup>3</sup> (K N et al., 2022). The pyrolysis gas has many potential applications, such as direct use for heat or electricity, co-firing applications with coal, production of individual gas components of interest, like H<sub>2</sub>, promoted by the use of catalyst, such as dolomite, ZnCl<sub>2</sub>, Ni/Fe that also improve the gas composition for eventual downstream applications (e.g. Fischer-Tropsch synthesis)(Kan et al., 2016b). The use of pyrolysis gas as an energy vector offers several advantages, including its renewable nature, potential for carbon neutrality and versatility in applications. However, challenges such as variability in composition, purification requirements (Paethanom et al., 2013), and scale-up of production processes need to be addressed to realize the full potential of pyrogas as a sustainable energy source.

## 2.4 BIOCHAR APPLICATION AS SOIL AMENDMENT

Amid the global shift towards technologies aimed at reducing atmospheric CO<sub>2</sub> emissions, biochar emerges as a particularly interesting option. Its simplicity sets it apart from other carbon capture and storage technologies, and its versatility allows for a broad array of applications across various fields

such as soil conditioning, wastewater treatment, sorbent technology, catalysis, feeding, construction, and more. Subsequent sections will investigate the specifics of biochar's use as a soil conditioner and its potential as a carbon removal technology.

#### 2.4.2 PRO AND CONS

The use of carbonaceous materials in the soil does not represent a novelty. Nowadays, the research on the use of biochar as conditioner provides interesting and promising results. Thanks to its chemical properties, such as high level of carbon and presence of nitrogen and pH and its physical properties, such as porosity and grain size it is able to enhance soil properties in several ways.

The application of biochar as soil amendment has the following advantages:

- The addition of biochar enhances the concentration of carbon in the soil. This has a beneficial effect on soil fertility and on soil adhesion (Watts & Dexter, 1998) and improves microbial activity in the soil. Cation exchange capacity improvement (Brassard et al., 2019).
- The Nitrogen content of biochar can improve the crop yield and quality of the production.
- Ash: the inorganic fraction of biochar contains inorganic plant nutrients such as Ca, Mg, K and P (Huygens et al., n.d.)
- Ph: the addition of biochar can increase the alkalinity of the soil; however, studies demonstrate that the effectiveness of biochar as liming agent is limited compared to commercial fertilizers (Huygens et al., n.d.)
- Porosity: the introduction of such a porous material within the soil improves the overall porosity of the soil, thus, causing a decrease soil bulk density and packing reduction. Moreover, it significantly increases the water retention capability of the soil. Improves nutrients soil retention reducing the leaching effect (Huygens et al., n.d.).
- Grain size: the small particles size of biochar facilitates the use as soil amendment.

The studies done by Kavitha et al. and Amalina et al. (Kavitha et al., 2018) (Amalina et al., 2023), highlight possible drawbacks associated with the use of biochar as soil amendment:

- Biochar has an inhibitory effect on soil aging, affecting nutrient cycling and soil health.
- Biochar effectiveness as soil amendment depends on starting biomass.
- Benefits of biochar are soil specific and plant specific.
- Biochar can react with soil nutrients to act as competitor.
- Biochar cost depends on availability of the initial feedstock.
- Affect the profusion of earthworm, precious for soil ecosystem.
- Delay in flowering for plants.
- Large use of biochar in soil tends to make surface darker, reducing surface Albedo, increasing the soil temperature.

#### 2.4.3 BIOCHAR REQUIREMENT FOR SOIL APPLICATIONS

The European Commission has established a set of criteria that biochar, its production process, and the input feedstock must adhere to before being utilized in soil applications (Huygens et al., n.d.):

- Biomass input material used must belong to a specified list of feedstocks.
- Eventual additives (catalyst) employed must belong to a specified list and has to be limited in quantity (<25%).
- Requirements related to preprocessing of feedstock.
- Requirements on process conditions.
- H/C<sub>org</sub> molar ratio < 0.7, with testing to be performed in the dry and ash-free fraction for materials that have an organic C content of < 50%. Such value defines the required level of stability of the carbon present in biochar, guaranteeing that the level of VOC and pyrolysis liquid contamination present in the biochar are below the limit that could cause phototoxic effect and adverse effects on aquatic organisms.
- Chloride levels in biomass <2%, due to adverse effects on environments.
- Mn content of biomass >3,5% shall be labelled.
- PAHs<sup>4</sup> (16 US EPA congeners, mg kg<sup>-1</sup> dry matter): < 6%.
- PCDD/F<sup>5</sup> (ng WHO toxicity equivalents kg<sup>-1</sup> dry matter): < 20.
- DL-PCB<sup>6</sup> (sum of 6 congeners PCB 28, 52, 101, 138, 153, 180, mg kg<sup>-1</sup>): < 0.2%.

## 2.5 CARBON OFFSET CREDITS

Article 6 of the Paris agreement specifies that nations to collaborate voluntarily in order to fulfill emission reduction goals outlined in their NDCs (Nationally Determined Contributions), opening the possibility to create a market of Carbon offset Credits.

The Carbon offsetting is a trading mechanism that allows to compensate greenhouse gas emissions; in other words, an entity (whether governments, businesses or individuals), exceeding greenhouse gas emissions limits, can offset part of its emissions through the acquisition of carbon credits sold by an entity that reduce, avoid, or remove emissions elsewhere. Carbon credits are generated through a certification procedure done by a government or an independent certification body; it represents the reduction, avoidance or removal of a ton of carbon dioxide or equivalents from the atmosphere.

### 2.5.2 PURO EARTH STANDARD

The application of biochar to the soil has two potential implications: the first, soil conditioning, improving physical and chemical characteristics of the soil, with beneficial effects on agriculture; the second, the sequestration of carbon for long period (> hundred year), preventing the emission of CO<sub>2</sub> in the atmosphere, acting as effective climate change mitigator.

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<sup>4</sup> Polycyclic aromatic hydrocarbons can be formed during pyrolysis process, are soil contaminant.

<sup>5</sup> Dioxins and furans can be formed during pyrolysis process, are soil contaminant.

<sup>6</sup> Dioxin-like polychlorinated biphenyls can be formed during pyrolysis process, are soil contaminant.

To assess and certify the effectiveness of biochar as stable carbon storage mean is necessary to undertake a certification procedure by a certification entity, among the more relevant appear Puro Earth, Verra and European Biochar Certificate.

Puro Earth platform brings together suppliers of carbon-net-negative technologies and climate-conscious companies. They issue verified CO<sub>2</sub> Removal Certificates (CORCs) based on the Puro Standard. Puro Standard is the first standard for carbon credits based on the carbon removed from the atmosphere and stored long-term (>100 year) in carbon net-negative processes or products. The methodologies of the Puro Standard are science-based and durable, and therefore dependable for precise compensation of emissions.

According to Puro Standard, biochar utilized as a soil conditioner must meet various specifications. These include being derived from sustainable biomass, with a production process engineered meticulously to prevent methane emissions into the atmosphere. Biochar itself must exhibit a H/Corg ratio of less than 0.7 to be deemed stable, and it must satisfy any jurisdictional product quality standards applicable to its usage and specific applications. Additionally, the product's overall negative impact should be assessed via a Life Cycle Assessment.

### 3 CASE STUDY: PRODUCTION AND USE OF BIOCHAR AS SOIL CONDITIONER WITH CARBON OFFSET CREDITS.

The commitment consists of a series of 9 experiments: 7 slow pyrolysis tests conducted in a horizontal batch reactor, with temperature ranging from 350°C up to 650°C, with 50°C steps, to obtain the optimal conditions for biochar production. Once the optimal conditions are established, 2 repetitions of the best run are performed with a large scale continuous horizontal mechanically fluidized bed reactor to obtain the biochar for the following application investigated in this thesis.

#### 3.2 METHOD: BATCH MODE

##### 3.2.1 BIOMASS

This study is based on the valorization of cocoa beans shell, an agro-industrial product residue of food factory specialized in the processing of cocoa. The biomass comes to ICFAR as raw mixture of cocoa shells and cocoa-based process powders (almost 60% of the mass), an initial sieving is therefore needed to separate the two fractions. The cocoa shells will be the object of this investigation, no interest has been given to process powders.



Figure 10 Raw biomass composition

The properties of the biomass are represented in the following table, Table 5.

Table 5 Properties of Cocoa Shells

Characteristic	Cocoa bean shell
Bulk Density (kg/m <sup>3</sup> )	170

Particle size (cm <sub>2</sub> )	1-2
Moisture content (%wt)	5 % – 9 %
Volatile Matter (wt% DB)	70 %
Ash content (wt% DB)	8,2 %
Fixed Carbon (wt% DB)	22 %

Moreover, an elemental analysis has been performed to assess the composition of the biomass in terms of C, H, N, S and O, the results are summarized in Table 6.

Table 6 Elemental composition of Cocoa Shells.

Elemental composition	%wt DB
C	49.5
H	5.5
N	2.5
S	42.4
O <sup>7</sup>	0.0

It is important to underline that besides the physical-chemical characteristics of the biomass, another important factor that defines the techno-economic feasibility of pyrolysis project is the availability of the material around the year. Hence, the minimal moisture content and decreased particle size (around 1 cm<sup>2</sup>) facilitate convenient handling and storage. Coupled with its year-round availability, these characteristics render this feedstock especially conducive to pyrolysis processes.

Prior to the experiments the feedstock is stored at ambient temperature and ambient air moisture.

### 3.2.2 BATCH PYROLYSIS SET-UP

The Horizontal Unit (HU) is a lab-scale batch horizontal mechanically fluidized bed reactor for slow pyrolysis, its reduced dimensions permit an easy control of process parameters and facilitate the execution of the tests. It consists of an insulated stainless-steel horizontal cylindrical chamber of 15 L equipped with an induction heater and two thermocouples, one located beneath the reactor bed and the other at the outlet of the gases. The bed is mechanically fluidized by means of a mixer shaft operated by an electric motor. A stream of 2 L/min of N<sub>2</sub> is injected to create an inert ambient and to remove the produced vapors that are eventually cooled down by two series-connected water condensers, enabling the separation of the liquid product. The uncondensed gas fraction passes

<sup>7</sup> The oxygen content is obtained subtracting the composition of the other elements and ashes.



through a cigar filter prior to reaching a collection point, an analogic flow meter, and ultimately, the ambient exhaust. A representation of the reactor is proposed in Figure 11.

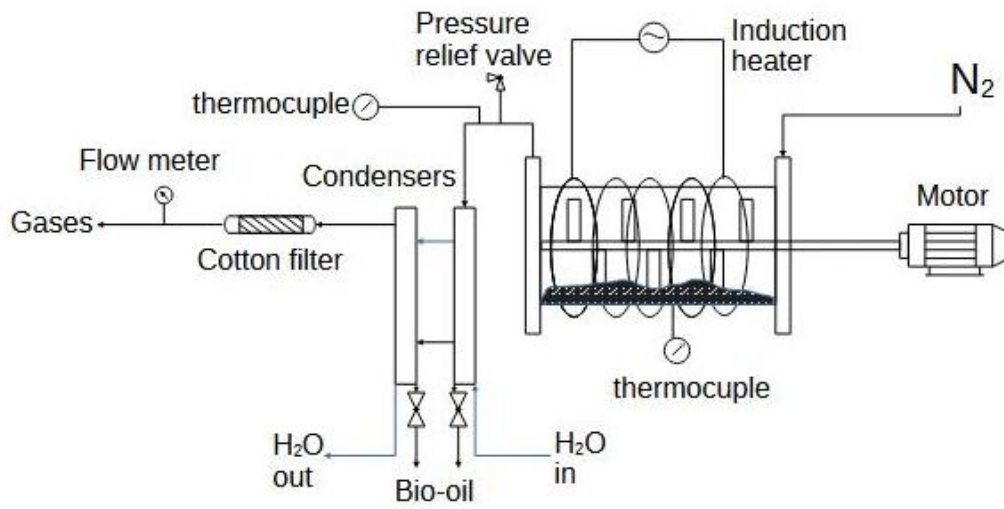


Figure 11 Schematic representation of the Horizontal Unit pyrolysis set-up

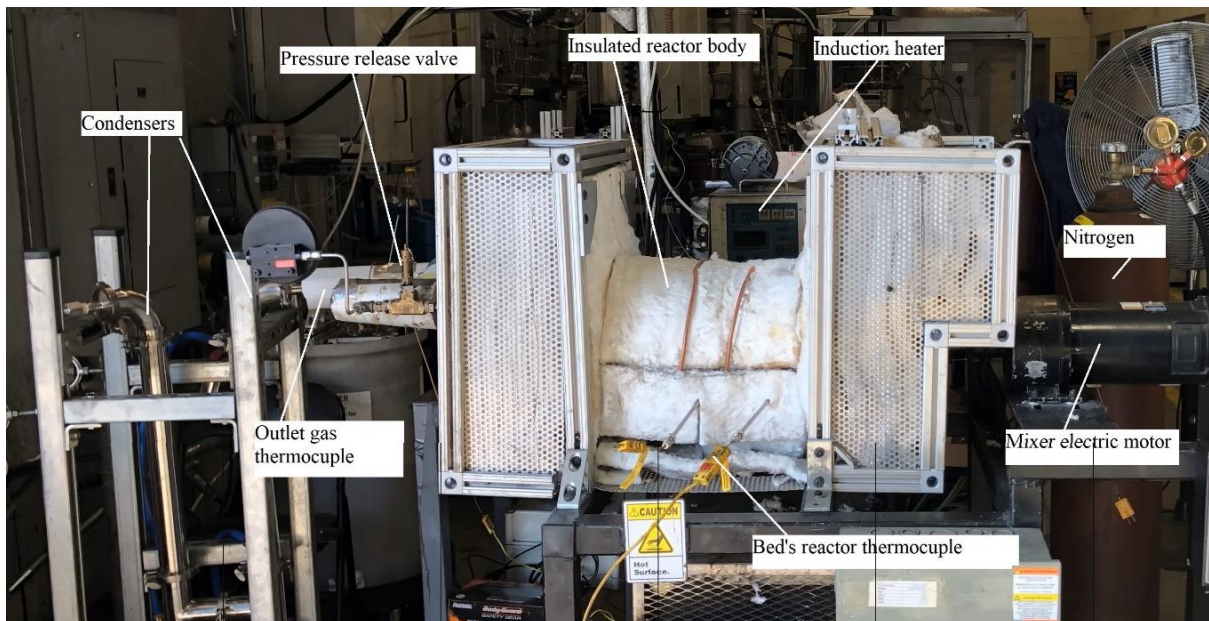


Figure 12 Horizontal Unit pyrolysis set-up



Figure 13 Internal chamber of Horizontal Unit batch reactor

### 3.2.3 EXPERIMENTAL PROCEDURE

For each run, 1 kg of feedstock is manually introduced inside the reactor, then, chamber is closed and the N<sub>2</sub> is injected to establish an inert atmosphere. The induction heater provides heat at around 30°C/min; once the operating temperature is reached, ranging between 350°C and 650°C depending on the experiment, the mixer is activated and the temperature is maintained for 1 h (residence time). Eventually, the heater is turned off and the reactor is left cooling keeping the N<sub>2</sub> flow until the bed temperature is below 300°C. Three gas samples are collected during each run (at 15, 30, 50 minutes after the target temperature is reached). To assess the liquid fraction production, in addition to condensers production, all the components downstream of the condenser (pipe line and cigar filter) have been considered. The biochar, on the other hand, is retrieved from the reactor chamber when it is reopened for cleaning procedures.

In total 7 experiments were performed with this equipment, keeping the same operating procedure, and changing the operating temperature: 350, 400, 450, 500, 550, 600, 650 °C.

The features of the batch process and HU are summarized in the following table, Table 7.

Table 7 Reactor characteristics.

Reactor	Horizontal Unit
---------	-----------------

<b>Dimensions (cm x cm)</b>	20 x 46
<b>Mode of operation</b>	Batch
<b>Productive Capacity</b>	1 kg/run
<b>Heating Rate</b>	~30°C min <sup>-1</sup>
<b>Operating Temperature</b>	300°C- 650°C
<b>Solids RT</b>	1 hour
<b>Heating Method</b>	Direct, Induction Heater
<b>Loading</b>	Manual
<b>Final Product Targeted</b>	Char
<b>Operating Pressure</b>	1 psig
<b>Material</b>	Stainless Steel
<b>Mixer shaft speed</b>	30 rpm

### 3.2.4 PRODUCTS CHARACTERIZATION

#### 3.2.4.1 SOLID

The characterization of solid products consists of elemental and proximate analysis. The elemental analysis was conducted using a Thermo Flash EA 1112 unit; samples undergo combustion at 900°C within a helium atmosphere with a regulated quantity of oxygen. The gases generated during combustion are subsequently examined in a chromatography-packed column. The elemental composition, including carbon, hydrogen, nitrogen, and sulfur is determined, while the oxygen content is calculated based on the difference (Laghezza, 2021). The proximate analysis, instead, involves the determination of moisture, volatile matter, fixed carbon, and ash content.

The proximate analysis is based on the following procedure (Laghezza, 2021):

- 1- Moisture evaporation from crucibles in a muffle at 750°C for 10 minutes.
- 2- 1 g of sample is added to the crucible, then dried for one hour at 105°C.
- 3- 7 minutes at 950°C with partial lid covering, for volatile matter devolatilization.
- 4- 4 hours at 450 °C without lid to define the ash content.

After each step the samples are weighted and the parameters are computed as described below:

### 3.3 RESULTS: BATCH MODE

### 3.3.1 YIELDS

As expected, the slow pyrolysis of cocoa shell originated three products: (1) the char, black and brittle carbonaceous material; a (2) double phase liquid, made up by minor oil fraction and a significant water fraction and (3) the remaining amount of non-condensed gases. Figure 14 shows the solid and liquid fraction obtained from the process.



Figure 14 Solid and liquid products from slow pyrolysis of cocoa shells

Figure 15 represents the yields of biochar at different temperatures. In accordance with the literature, the yield shows a decreasing trend with the increase in the maximum operating temperature, indicating that temperature has a significant impact on the char yield. At 350°C the solid fraction counts for the 65%, this value, certainly higher than the ranges described in literature, is justified by the presence of unreacted material in the solid sample (Figure 16), suggesting that longer residence time would be recommended for such temperature. Instead, at 400°C the yield is 49%, decreasing up to 33% at 650°C; it is evident that the rate of change of the yield is higher in the range of temperature 350-500°C, while decreases in the range 500-650°C unveiling an asymptotic pattern at approximately 30% of char yield.

Figure 17 represents the yield of liquid products, the values range from 16% (wt%, DB) at 350°C up to 39% (wt%, DB) at 550°C, the values align with existing literature, taking into account the low initial moisture content of the biomass; the low production obtained at 350°C is again related to the incomplete decomposition of the feedstock. The parabolic trend is perfectly in line with the theoretical predictions, moreover, the presence of an absolute maximum at 550°C reveals that the secondary decomposition reaction becomes predominant above that temperature, resulting in a decrease of the liquid yield and a corresponding increase of gas yield, as reported in Figure 18.

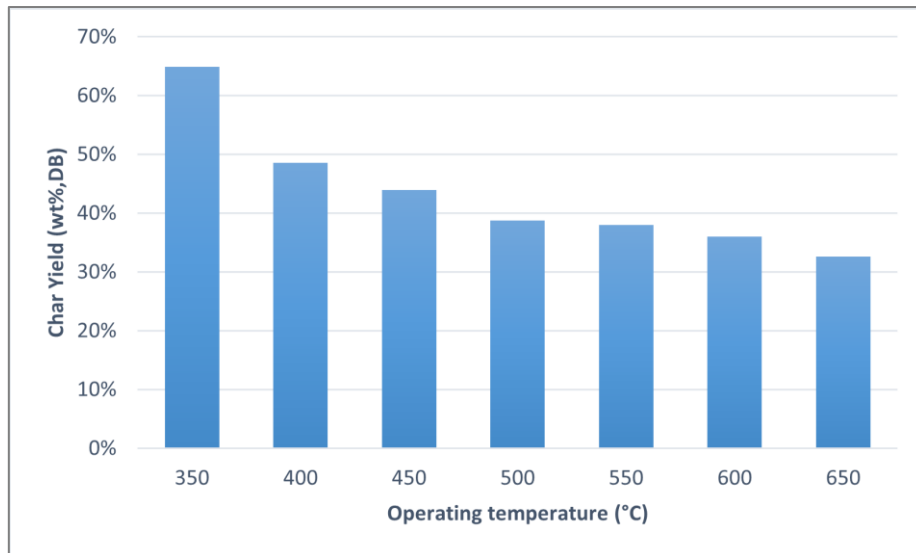


Figure 15: Biochar yield with vs Maximum Operating Temperature



Figure 16: Detail of solid unreacted material obtained at 350°C for 1 hour

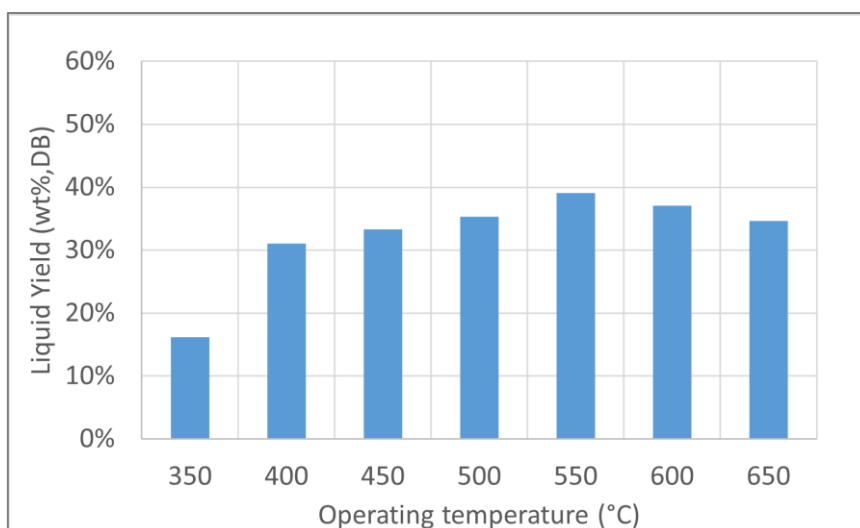


Figure 17 Liquid Yield vs Maximum Operating Temperature

The gas yield is obtained by difference, subtracting solid and liquid yields.

The production range between 19% at 350°C and 33% obtained at 650°C; the values are in line with the literature, defining an increase of the yield with increasing temperatures, as a consequence of the progressive increase in the gasification reactions. It is interesting to notice the presence of a peak at 500°C, this is consequence of the relatively longer residence time used in that test (1,6 hours) that lead to a more complete decomposition of the biomass, which increased the gas yield.

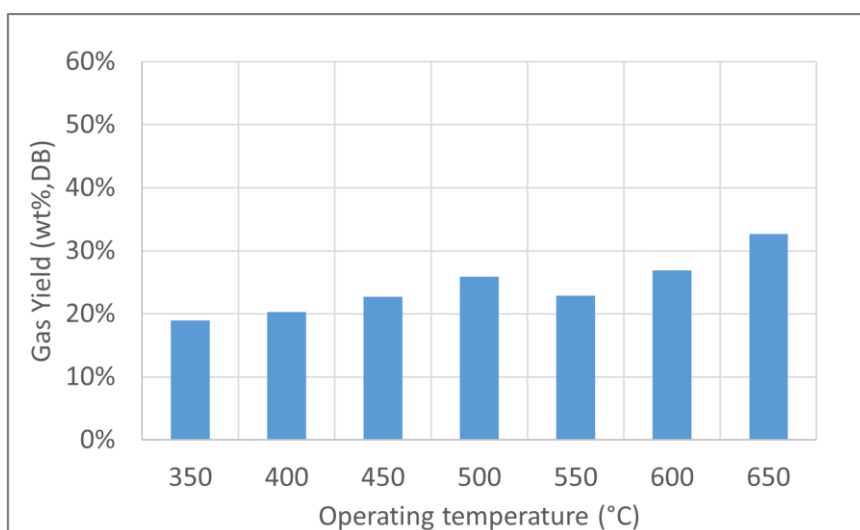


Figure 18 Gas Yield vs Maximum Operating Temperature

### 3.3.2 SOLID

The biochar represents the main product of interest of this study; proximate and elemental analyses were conducted to evaluate its quality and determine the ideal conditions for further continuous mode testing. Table 8 describes the results of the proximate analysis.

Table 8: Proximate analysis of biochar from pyrolysis of cocoa shells processed at different temperatures

Temperature (°C)	Volatile matter (% DB)	Ash content (% DB)	Fixed Carbon (% DAFB)
350	49,8	15,9	34,3
400	28,5	18,8	52,7
450	27,1	18	54,9
500	13,4	21,6	65,0
550	12,7	22,5	64,8
600	10,2	22,1	67,7
650	3,8	25,1	71,1

Table 8 shows that the content of volatile matter in the biochar samples decreases with the increase in temperature, this is consequence of the enhancement of devolatilization reactions occurring at higher pyrolysis temperatures. The relative ash content in the samples increases shows an increase with pyrolysis temperatures. The amount of fixed carbon is obtained as difference of the previous parameters and moisture content; it shows an expected increasing trend consequence of the increase in pyrolysis temperature, again associated with the promotion of decomposition of volatiles compounds and organic matter, leaving a higher proportion of carbon behind in the form of fixed carbon in the biochar.

As the pyrolysis temperature increases, the elemental composition of the resulting biochars is shifted from that of the initial feedstock biomass to compounds with higher carbon content and lower hydrogen content. Table 9 shows the elemental composition of the biochar obtained at different temperatures.

Table 9 Elemental composition of biochar samples, temperature ranging between 350 and 650°C, %wt DB.

Temperature (°C)	C	H	N	S	O
350	68,7	5,9	5,2	0,0	20,2
400	80,6	4,6	4,2	0,0	10,6
450	83,1	4,0	3,6	0,0	9,2
500	86,1	1,7	1,9	0,0	10,4
550	88,2	1,6	2,3	0,0	8,0
600	87,5	1,4	2,8	0,0	8,3
650	92,5	0,9	2,7	0,0	3,9

Figure 19 quantify the share of recalcitrant carbon of the biochar through the H/C molar ratio; the H/C ratio is an indicator of the overall biochar stability in the soil (Ronsse et al., 2013). According to Lehmann et al. study on persistence of biochar in the soil, values of H/C ratio lower than 0,4 ensure that more than 90% of biochar initial carbon content will remain after 100 years (Lehmann et al., n.d.). According to Puro Earth Biochar standard, the molar ratio H/C must be lower than 0,7 for environmental applications (Schimmelpfennig & Glaser, 2012a). In this study, such thresholds are overcome for pyrolysis temperature higher than 450°C, Figure 19.

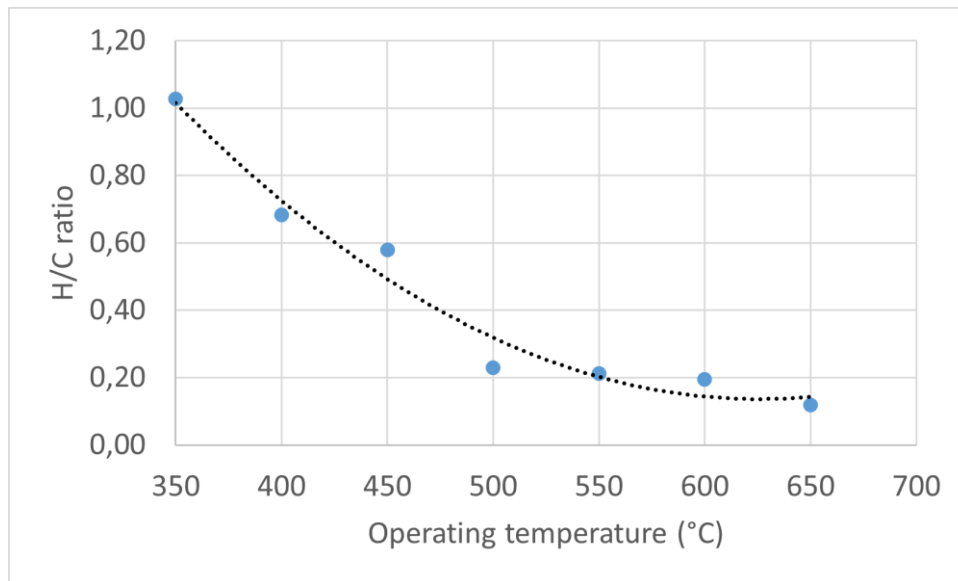


Figure 19 H/C ratio vs pyrolysis operating temperature.

According to the result obtained with the HU setup, the test at 500°C results to be the optimal condition for slow pyrolysis of cocoa shells since the H/C ratio has a value lower than 0,4, featuring the highest relative decrease of H/C ratio between two consecutives temperatures, corresponding to 0,2, 60% less compared to the H/C ratio observed at 450°C. Moreover, 39% of biochar yield at 500°C represents the highest yield among the eligible tests (i.e. H/C molar ratio lower than 0,4).

### 3.4 METHOD: CONTINUOUS MODE

#### 3.4.1 PYROH SETUP

The second phase of production is carried out in continuous mode through a 75 L horizontal mechanically fluidized bed reactor (PyroH). The body is a stainless-steel insulated cylinder equipped with a ceramic heater controlled by two thermocouples located within the reactor bed. Inside, the bed is fluidized by means of a mixer shaft operated by an electric motor, an oxygen depleted environment is established through the injection of N<sub>2</sub>. The continuous feeding of fresh biomass (80 g/min) is carried by a screw conveyor that connects the 74 L feeding hopper to the reactor. The char is removed at the end of the chamber by a gravity mechanism while vapors go through two parallel condenser units operating at same temperature that cool down the stream enabling the separation of the liquid



fraction. Finally, the incondensable fraction is released into the ambient. The presence of a valve and cotton filter situated downstream of the condensers allows the collection of gas samples.

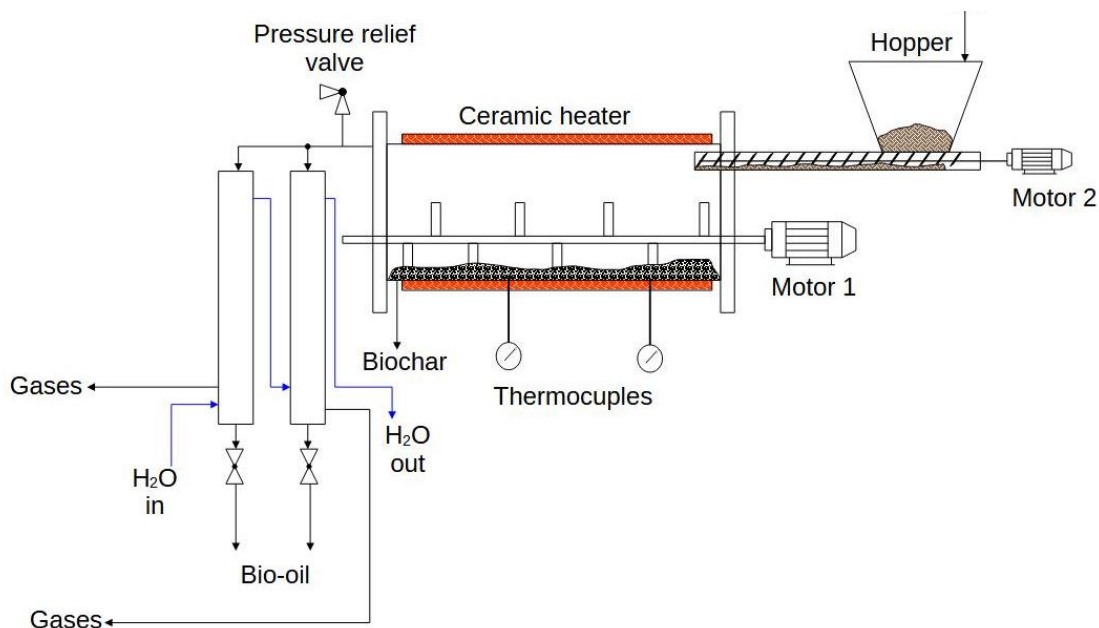


Figure 20 Schematic representation of PyroH pyrolysis reactor

Table 10: Pyroh pyrolysis reactor characteristics

Reactor	PyroH
<b>Dimensions (cm x cm)</b>	32 x 91
<b>Mode of operation</b>	Continuous
<b>Productive Capacity</b>	4,8 kg/run
<b>Heating Rate</b>	$\sim 30^{\circ}\text{C min}^{-1}$
<b>Operating Temperature</b>	500-600 °C
<b>Heating Method</b>	Direct, Ceramic Heater
<b>Loading</b>	Bed: Manual; Continuous feeding: screw mechanism
<b>Final Product Targeted</b>	Char
<b>Operating Pressure</b>	0,5 psig
<b>Material</b>	Stainless Steel

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**Mixer shaft speed**15 rpm

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### 3.4.2 EXPERIMENTAL PROCEDURE

Setting up the bed is essential for running in continuous mode, approximately 9 kg of feedstock are manually introduced in the reactor while around 7 kg of feedstock are inserted in the feeding hopper. Once all the components of the reactor assembly are completely sealed, an inert atmosphere is created through the injection of 10 L/min for 15 minutes. Then, the bed is prepared, the reactor is heated at 500 °C, 1,5 L/min of N<sub>2</sub> injected and the mixer is operated, in this phase the reactor works in batch mode: there is no introduction of fresh feedstock into the reaction chamber, nor is any char removed from it. After 1,5 hours, the bed material is completely converted into biochar and the actual continuous feeding can start. The continuous mode is operated until the hopper is empty, during this time the char collection system is in operation; gas samples are also collected through a gas sampling system located downstream the condensers. The gas sampling system is equipped with a cotton filter to remove the residual condensable compounds present in the gas. Eventually, ceramic heaters are turned off and the reactor is left cooling keeping the N<sub>2</sub> flow constant until the temperature of the bed is well below 300 °C. Finally, the biochar is collected through a sealed tank connected to the gravity collection system and the liquid fraction is extracted from tanks connected to the condensers.

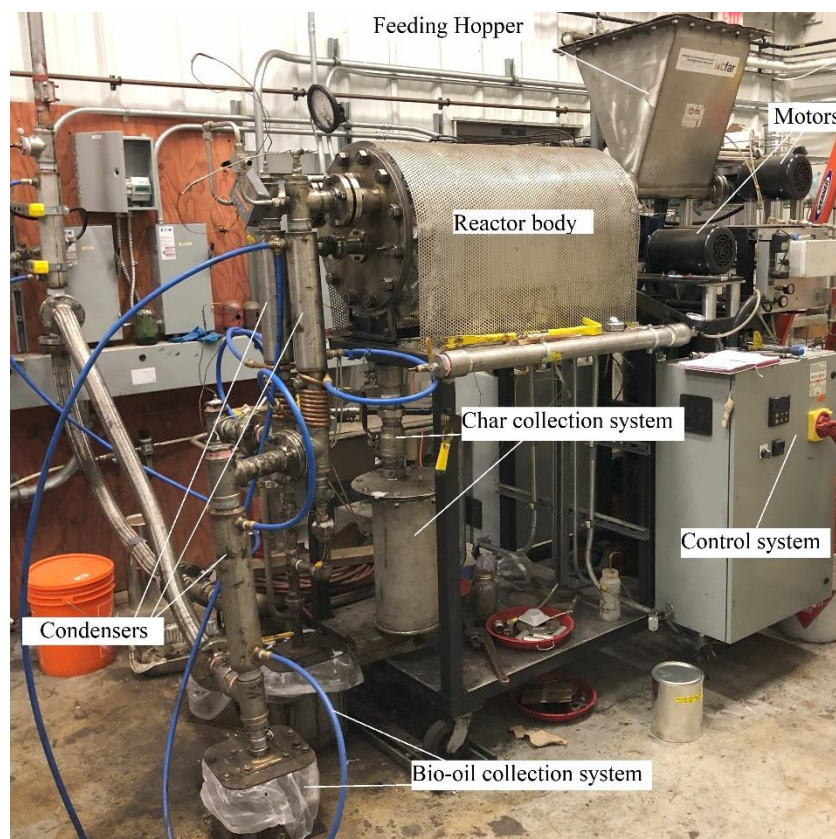


Figure 21: Pyroh, Continuous mechanically fluidized Pyrolysis reactor.

### 3.5 RESULTS: CONTINUOUS MODE

#### 3.5.1 YIELD

Inefficiencies in the collection system of oil and biochar prevent a clear understanding of the actual yields. Therefore, yields obtained through the test in batch at 500°C are considered for the following stages of the study, Table 11.

Table 11: Yields from pyrolysis of cocoa shells at 500°C.

class	Yield	
	[kg/100.kgBiomass daf]	Temp °C
<b>Biomass</b>	100	20
<b>Biochar</b>	39,0	500
<b>Dry-Biooil</b>	24,5	500
<b>Water</b>	10,5	500
<b>Gas</b>	26,0	500

#### 3.5.2 SOLID

The characterization of the solid fraction follows the same procedure described in the batch operations. Table 12 describes the result obtained from the proximate analysis, while Table 13 represents the elemental compositions.

Table 12: Proximate composition of biochar obtained in continuous mode.

Temperature (°C)	Volatile matter (% DB)	Ash content (% DB)	Fixed Carbon (% DAFB)
500	11,8	24,8	63,3

Table 13: Elemental composition of biochar obtained in continuous mode, wt% DB.

Temperature (°C)	C	H	N	S	O	H/C	O/C
500	86.1 %	1.7 %	1.9 %	0.0 %	10,4 %	0.231	0.090



Figure 22: Biochar obtained in continuous mode at 500°C.

### 3.5.3 GAS

The analysis of the composition of non-condensable fraction of gasses of the pyrolysis of cocoa shells is performed using a micro gas chromatographer (Varina mobile CP-4900). This unit is equipped with a column module containing a molecular sieve and a polar plot unit to identify  $H_2$ ,  $CH_4$ ,  $CO$ ,  $CO_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $H_2S$ ,  $SO_2$ ,  $C_3H_6$ ,  $C_3H_8$ ,  $C_4H_{10}$ ,  $C_5H_{12}$ , and  $C_6H_{14}$ . The thermal conductivity detector (TCD) uses helium and argon as carrier gasses at a pressure of 80 psi. Each sample is analyzed three times, and the average is calculated to estimate the concentration. Figure 23 shows the resulting composition.

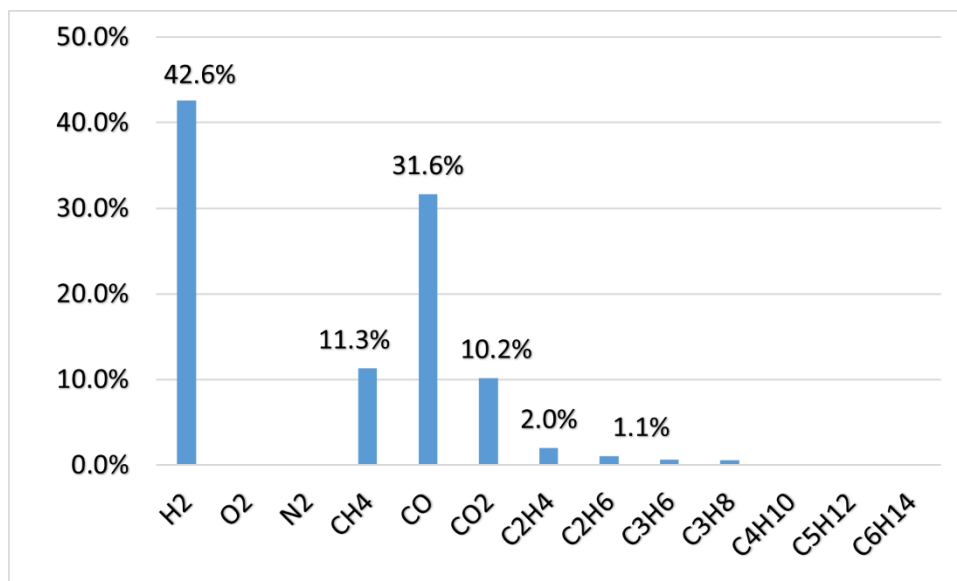


Figure 23: Gas composition (%vol) from continuous pyrolysis of cocoa shells at 500°C (Vaštyl et al., 2022).

### 3.5.4 LIQUID

The resulting product from the condensation of pyrolysis vapors result to be a mixture of heavy oil and a watery fraction rich of organic compounds (e.g. acetic acid, formic acid, furfural, hydroxyacetaldehyde, levoglucosan methanol, phenol (Mohan et al., 2006b)). To understand the elemental composition of the overall liquid mixture an indirect approach has been followed: starting with the elemental composition of the initial biomass, of the biochar and of the gases and applying a mass balance the resulting elemental composition of the liquid fraction has been evaluated, Table 14.

Table 14: Elemental composition of the products obtained from pyrolysis of cocoa shells at 500 °C, wt%.

class	Yield [kg/100. kgBdaf]	Temp °C	C	H	N	O	S
<b>Biomass</b>	100	25	49,5%	5,5%	2,5%	42,4%	0,0%
<b>Biochar</b>	39,0	500	86,1%	1,7%	1,9%	10,4%	0,0%
<b>Dry-Biooil</b>	24,5	500	19,1%	5,8%	7,3%	67,8%	0,0%
<b>Water</b>	10,5	500	0,0%	11,1%	0,0%	88,9%	0,0%
<b>Gas</b>	26,0	500	43,4%	8,8%	0,0%	47,7%	0,0%

## 4 CARBON CREDITS ASSESSMENT

The last part of the study is related to the assessment of the Carbon Credit associated to the production of biochar from cocoa shells and its permanent application in the soil as amendment. In particular, the Life Cycle Analysis (LCA) performed is a simplified version, assessing only the contribution of CO<sub>2</sub> emission associated to assess the credits, instead of considering all the environmental impacts associated (i.e. acidification potential, eutrophication potential, ozone depletion potential, human toxicity...).

### 4.1 SIMPLIFIED LCA

#### 4.1.1 GOALS

This analysis is dedicated to the assessment of the CO<sub>2</sub> associated with the production biochar from cocoa shells and its application as soil amendment. The goal is to assess the net CO<sub>2</sub> emissions associated to define the amount of carbon credits generated according to the method adopted by Puro Earth standard (Schimmelpfennig & Glaser, 2012b).

#### 4.1.2 SCOPE

The biomass considered is a residue obtained from food industry, therefore Zero burden approach is used, hence, the starting point is the generation of the residue. All the impacts coming before need to be allocated to the main product. The burden is considered to start with the generation of the residue. According to that, the **overall system boundary** refers to the case B: **Cradle-to-Grave**, according to Puro standard (Schimmelpfennig & Glaser, 2012b). It is important to underline we refer as cocoa shells, a biomass residue, as Waste biomass according to Puro Methodology.

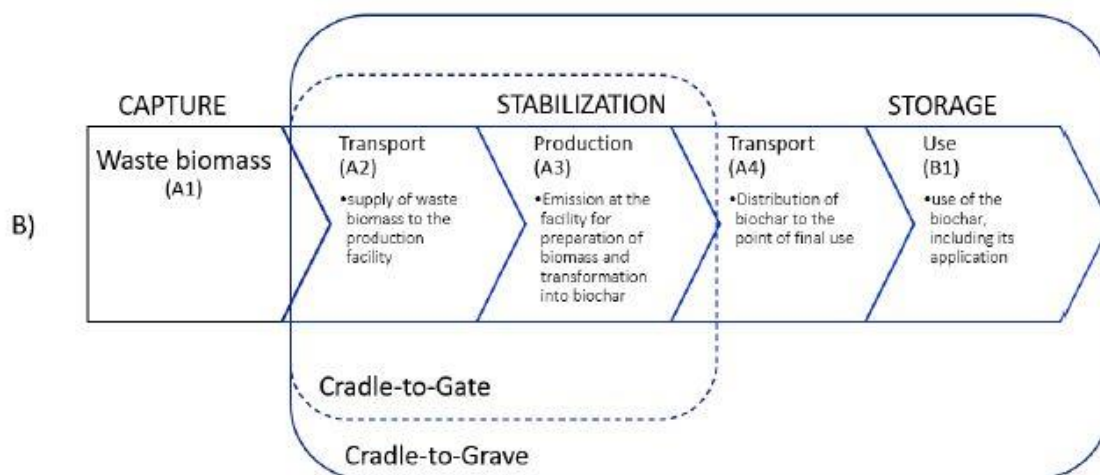


Figure 24: Gate-to-Grave system boundary for the assessment of biomass residues(Schimmelpfennig & Glaser, 2012b).

Consequently, the **activities under analysis** are:

- Transport: supply of biomass to the production facility, including vehicle and fuel and infrastructure emissions.
- Production: emission related to the preparation of biomass and transformation into biochar, operation of the process equipment, handling on site of the feedstock, packaging for final biochar product.
- Transport: distribution of biochar to the average point of final use, including vehicle, fuel and infrastructure emissions.
- Use: emissions associated with the use of biochar as soil amendment, including the handling.

Table 15: Product description.

Product	Description	Biochar Yield	Functional Unit
Cocoa shells biochar	Biochar obtained from slow pyrolysis of cocoa shells at 500°C.  Primary Function: carbon sequestration and soil conditioning.	39%	1 ton

The **Functional unit** selected is **one metric ton of biochar**, further product information is described in Chapter 3.

Assumptions and secondary data are required when information and primary data are not available. Missing information (emissions associated transportation, fuel, packaging) has been gathered through software Simapro, according to IPCC 2021 GWP100 V1.02 method. Parameter uncertainty, scenario uncertainty, and model uncertainty are factors that contribute to the constraints encountered when utilizing LCA.

The impact category assessed with this LCA is the Carbon footprint, including the direct and indirect emissions linked with the production and use of biochar as soil amendment.

## 4.2 CALCULATION METHODOLOGY FOR THE QUANTIFICATION OF CO<sub>2</sub> REMOVAL

Puro Earth provides carbon dioxide removal certificates (CORCs) generated from biochar production activity, and the methodology for calculating them is outlined as follows.

Overall equation for net carbon sequestration over 100 years (tonCO<sub>2</sub>-eq.):

$$CORCs = E_{STORED} - E_{BIOMASS} - E_{PRODUCTION} - E_{USE}$$

- $E_{STORED}$ : represents the amount of CO<sub>2</sub>-eq stably (over 100 years) stored within the biochar.
- $E_{BIOMASS}$ : lifecycle greenhouse gases associated to the production and supply of biomass to the production facility, including direct land use changes.

- $E_{PRODUCTION}$ : lifecycle greenhouse gas emissions arising from transformation of biomass into biochar, at production facility. Includes handling of material within the site, operation of process equipment.
- $E_{USE}$ : lifecycle greenhouse gas emissions coming from the use of biochar (soil amendment in this case), including the contribution of the distribution to the point of final use.

## 4.3 LCA METHODOLOGY

### 4.3.2 BIOMASS RESIDUE PRODUCT

As previously stated, this analysis follows a Zero burden approach. Being a biological residue product, all the emissions related to the production of the biomass are associated with the main product and therefore outside the scope of this analysis.

### 4.3.3 TRANSPORT TO THE PRODUCTION FACILITY

This considers the emissions arising from the transport of the biomass residues from the suppliers to the production facility. This analysis considers that the feedstock will be treated on site, the location of the production facility corresponds to the food factory where the cocoa shells are produced. Therefore, 1 km has been assumed as a reasonable distance to take into account eventual transport of material within the plant. Assumption: transportation performed by single unit transport truck, diesel powered Euro VI, for 7-16 metric tons (Simapro).

### 4.3.4 PRODUCTION

The production phase involves slow pyrolysis to obtain biochar, managing biomass and biochar onsite, and packaging the biochar. Biochar characteristics are based on the laboratory test performed with Pyroh reactor (Chapter 3), additional assumptions have been formulated to take into account the increased dimensions of an industrial scale reactor.

Table 16: Productivity and yields

Cocoa shells biochar		Source
Process rate	500 kg/h Dry biomass	(Beston Biomass Carbonization Machine, n.d.)
Biochar yield	39%	Pyroh Test
Biochar production	195 kg/h	



In particular, the lab equipment (Pyroh) per se is not representative of industrial-scale process. To overcome such limitation, an industrial-scale setup has been assumed according to commercially available pyrolysis setup (Beston Biomass Carbonization Machine, n.d.). The process comprises multiple steps:

- 1) Feedstock handling within the plant by means of forklift.
- 2) Mechanical pre-treatment to remove cocoa process powders from cocoa shells.
- 3) Preliminary drying process, the heat needed to evaporate the biomass moisture is supplied by the heat released during the combustion of pyrolysis vapors.
- 4) The Pyrolysis process in continuous mode, at 500°C, based on the operating principle of Pyroh reactor without the use of condensers.
- 5) Combustion of pyrolysis vapors through a burner to obtain energy to sustain the process (pyrolysis and drying process) and oxidize residual combustible materials such as light gases (hydrogen, methane and carbon monoxide) volatile organic compounds and particulate matter.
- 6) Char collection, cooling.
- 7) Packaging and handling.

Table 17: Mass balance of the pyrolysis process expressed in wt%, referred to 100 kg of dry biomass and the relative yields (Table 14) .

		C	H	N	O	S
mass balance	inlet biomass	49,5	5,5	2,5	42,4	0,0
	biochar	33,6	0,6	0,7	4,04	0,0
	gas	11,3	2,3	0,0	12,4	0,0
	Water	0,0	1,8	0,0	9,3	0,0
	biooil	4,7	1,4	1,8	16,6	0,0

Table 18: Pyrolysis stage energy balance calculations.

direction	class	Yield [kg/100. kgBdaf]	Temp °C	formation enthalpy kJ/kg	Specific enthalpy kJ/kg	Enthalpy kJ/kg	Enthalpy kJ/kg B-daf	HHV kJ/kg	HHV kJ/kg biomass
inlet	Biomass	100.0	25	-5133	0.0	-5133.2	-5133.2	-18995	-18995
outlet	Biochar	39.0	500	186	620.6	807.0	314.7	-30744	-11990

outlet	Dry-Biooil	24.5	500	-4092	40.6	-4051.4	-992.6	-10490	-2570
outlet	Water	10.5	500	-13435	1159.4	12275.4	-1288.9	0	0
outlet	Gas	26.0	500	-4937	1044.7	-3892.0	-1011.9	-21135	-5495

Table 19: Mass and energy streams of pyrolysis process.

class	mass kg/h	Enthalpy MJ/kg <sub>biomass</sub>
Biomass	500,0	19,0
Biochar	195,0	12,0
Dry-Biooil	122,5	2,6
Water	52,5	0,0
Gas	130,0	5,5

Table 20: Energy balance of pyrolysis process.

Energy flow	inlet MJ	outlet MJ
Energy in products		20,1
Energy in reactivities	19,0	
Energy reaction	2,2	
Energy Heating Biomass	1,1	
Energy Loss		2,2

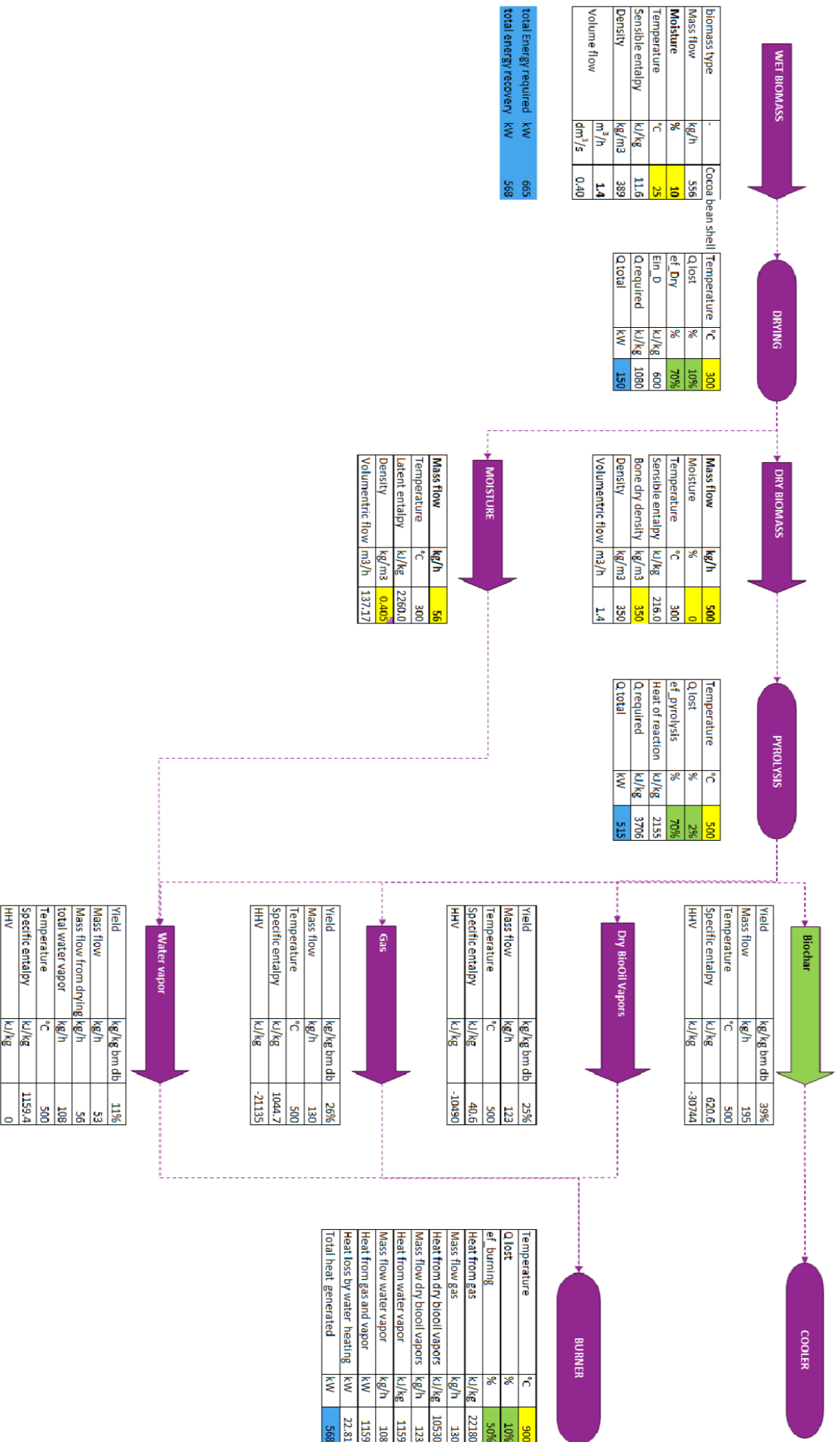


Figure 25 Energy balance of industrial scale pyrolysis setup concept based on Pyroh

The contribution of each step is taken into account in terms of energy requirements, then translated into tons of CO<sub>2</sub>-equivalent through the GWP conversion factors found in Simapro.

#### 4.3.5 TRANSPORT TO THE FINAL USE

This transport activity involves the transport of biochar from the production facility to the final user (soil conditioner). Even though the production plant is in an area with abundance of cultivation, an average distance of 100 km has been considered to take into account a broad network of potential biochar users. Assumption: transportation performed by single unit transport truck, diesel powered Euro VI, for 16-32 metric tons (Simapro).

#### 4.3.6 USE

The final use of cocoa shells biochar is as soil amendment. In this way the carbon will be securely stored in the soil, acting as long-term carbon removal technology and improving the physical and chemical properties of the ground. The emissions associated with this phase are related to the distribution of biochar on the field by means of tractors and the disposal of packaging.

### 4.4 CALCULATION PROCEDURES

#### 4.4.2 Estored CALCULATION

$$E_{stored} = Q_{biochar} \times C_{org} \times F_p^{TH:Ts} \times \frac{44}{12}$$

Where:

- $Q_{biochar}$ : represent the amount of biochar produced over the reporting period. It is expressed in dry metric tons of biochar.
- $C_{org}$ : organic carbon content of the biochar produced; it is expressed in dry weight of organic carbon over dry weight of biochar.
- the factor  $\frac{44}{12}$  is the ratio between the molar mass of carbon dioxide and the molar mass of carbon. This factor converts an amount of carbon to its corresponding amount of carbon dioxide.
- $F_p^{TH:Ts}$ : is the permanence factor of biochar organic carbon over a given time horizon  $TH$  in a given soil at temperature  $TS$ .

$$F_p^{TH:Ts} = c + m \times H / C_{org}$$

The regression coefficients  $c$  and  $m$  are a function of the time horizon  $TH$  and the soil temperature  $TS$ . Table 1 described in Puro Earth methodology provides the values of these two coefficients for a time horizon  $TH$  of 100 years, and for a range of soil temperatures  $TS$ . According to the plant location,

south Ontario (CA), where the average soil temperature is around 10°C (Zhang et al., 2005) we select the value 1,10 and -0,59 as c and m, respectively.

#### 4.4.3 Etransport CALCULATION

- Transportation of cocoa shell biomass from supply zone to production zone, within the same plant, in kgkm/tons biochar:

$$\text{Transportation (kgkm/tons biochar)} = \text{Biomass(kg/tons biochar)} * \text{Distance(km)}$$

#### 4.4.4 Eproduction CALCULATION

- Material Handling: Propane fueled Forklift, propane per tons biochar production:

$$\text{Propane (lbs/tons biochar)} = \text{Propane (lbs/day)} / \text{biochar production (tons/day)}$$

- Pre-treatment mechanical sieving: Electricity use per day per ton biochar production:

$$\text{Electricity (kWh/ton biochar)} = \text{Electricity use (kWh/day)} / \text{biochar production (tons/day)}$$

- Electricity supply for additional power components: Electricity use per day per ton biochar production:

$$\text{Electricity (kWh/ton biochar)} = \text{Electricity use (kWh/day)} / \text{biochar production (tons/day)}$$

- Packaging: Super sacks (polypropylene) use per ton biochar production:

$$\text{Super sacks (kg/ton biochar)} = \text{Super sacks (kg/day)} / \text{biochar production (tons/day)}$$

#### 4.4.5 Euse CALCULATION

- Transportation of biochar from production plant to End-User:

$$\text{Transportation (kgkm/tons biochar)} = \text{Biochar(kg/tons biochar)} * \text{Distance (km)}$$

- Packaging disposal: Super sacks (polypropylene) use per ton biochar production:

$$\text{Super sacks (kg/ton biochar)} = \text{Super sacks (kg/day)} / \text{biochar production (tons/day)}$$

## 4.5 RESULTS

Calculations to obtain Estored are reported in Table 21.

Table 21: Calculation of Estored, Equivalent tons of CO<sub>2</sub> stored in the biochar applied in a soil at 10°C.

	$Q_{\text{biochar}}$	$C_{\text{org}}$	$H$	$H/C_{\text{org}}$	Coefficient c	Coefficient m	$FpTH, Ts$	Estored
Biochar (10°C)	dry tons	%	%	mol/mol	-	-	%	tons CO <sub>2</sub>

<b>Cocoa bean shell</b>	<b>1</b>	86,1%	1,7%	0,2	1,10	-0,59	<b>96,4%</b>	<b>3,0</b>
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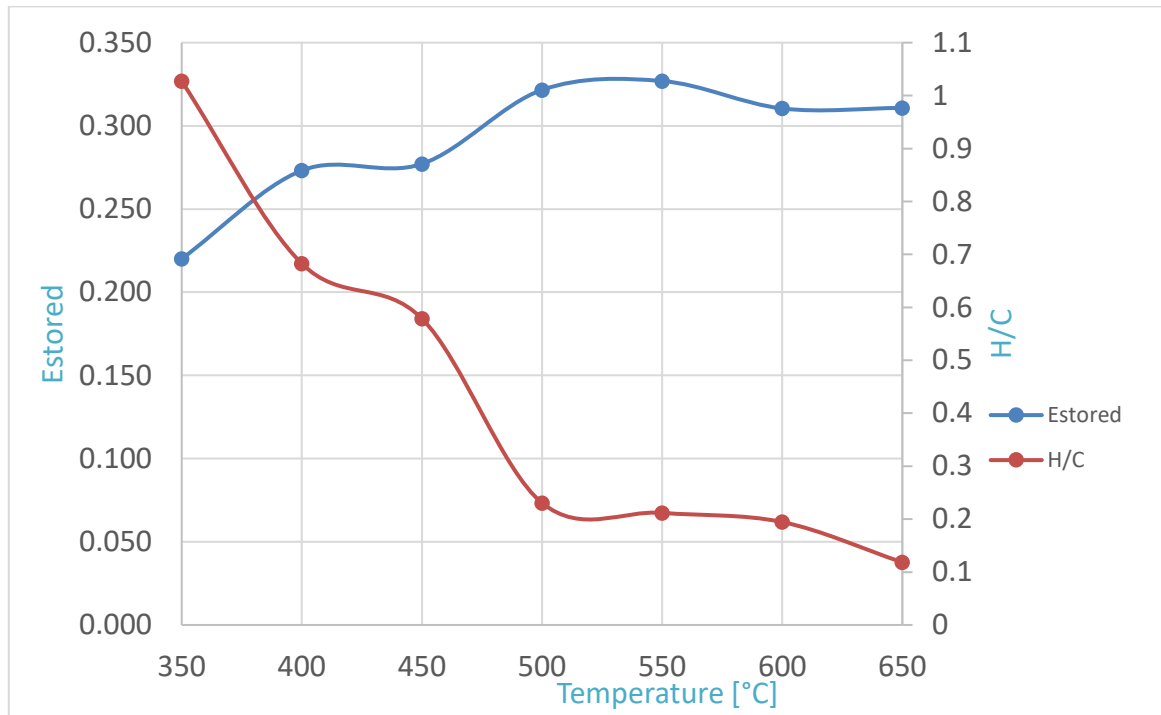


Figure 26: Variation of Estored and H/C ratio vs Pyrolysis temperature.

Figure 26 describes the variation of Estored, according to different pyrolysis temperatures done in the batch test. It is revealed that in the temperature range between 500-550 °C an absolute maximum is present.

Table 22: Calculation of Ebiomass.

LCI System Inputs and Outputs	Data	Unit	Comments	Data	Units per ton biochar	Data	Units per ton biochar	E Biomass
Cocoa nutshells	13,3	tons per day		<b>2,8</b>	tons			
Truck	1,00	Km	Treated on site	<b>2849</b>	kgkm	<b>0,7</b>	kg CO <sub>2</sub> -eq	<b>0,00069</b>
Cocoa nutshells biochar	4,7	tons per day		<b>1,0</b>	tons			

Table 23: Calculation of Eprod.

			Study Data			Converted Data		Data	Units per ton biochar
LCI System Inputs and Outputs			Data	Unit	Info	Data	Units per ton biochar		
LCI Inputs	Feedstock	Biowaste	13,3	Tons per day		2,8	tons		
		Pre-treatment stage	36	kWh per day	mechanical sieving	7,7		0,2	
	Forklift	Propane	60	lbs per day		12,8	lbs	5,6	
	Packaging	Super Sacks (Polypropylene)	23,9	kg per day	35" x 35" x 60" bag, 55 cu. ft; weighs 2.55 kg each. Capacity 500kg	5,1	kg	11,6	
		Energy Supply	432,0	kWh per day	Additional components	92,3	kWh	17,4	
LCI Outputs	Direct Air Emissions	Calculated CO <sub>2</sub> emissions	-	kg per day	Biogenic emissions	-	kg		
	Biochar	Biochar	4,7	tons		1,0	tons		
								34,8	kgCO <sub>2</sub> eq
TOTAL (minus biogenic)								0,03	ton CO <sub>2</sub> -eq.

Table 24: E<sub>use</sub> evaluation

LCI System Inputs and Outputs	Data	Unit	Data	Units per ton biochar	Data	Units per ton of biochar
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<b>LCI Inputs</b>	Biochar	Biochar	4,68	tons per day	<b>1</b>	tons		
	Transport	Truck	100	km	<b>100000</b>	kgkm	<b>19</b>	<b>kg CO<sub>2</sub>-eq</b>
	Packaging Disposal	Super Sacks	24	kg for day	<b>5</b>	kg	<b>8</b>	<b>kg CO<sub>2</sub>-eq</b>
<b>GWP, Use</b>							<b>27</b>	<b>kgCO<sub>2</sub> eq for utilization stage</b>
<b>Euse</b>							<b>0,03</b>	<b>tons CO<sub>2</sub>-eq.</b>

Table 25: Calculation of CORCs

		<b>CORCS</b>	Estored	Ebiomass	Eprod.	Euse
10 °C	<b>Cocoa nutshells biochar</b>	<b>2,98</b>	3,042	0,000689	0,035	0,027

As can be seen from the tables above, the pyrolysis of biochar and the consequent application as soil amendment offers the incredible advantage of being an efficient tool for carbon storage. According to the preliminary LCA performed in accordance with Puro Earth methodology, the biochar from cocoa shells is able to remove a net of 2,98 CO<sub>2</sub>-equivalent per ton of biochar. The main contributions are E<sub>production</sub> and E<sub>use</sub>, mainly associated with the use of fossil fuels (propane and diesel).

#### 4.6 COMPARATIVE WITH BESTON PYROLYSIS EQUIPMENT

In order to assess the consistency of the LCA study performed above, an additional preliminary LCA has been carried out considering an actual commercially available pyrolysis equipment provided by BESTON.

The manufacturer describes the equipment as:

“The equipment uses agricultural and forestry residues rich in lignin, cellulose and hemicellulose (such as straw, sawdust, rice husk, fruit shell, coconut shell, palm shell, tree bark, logs, firewood bars, palm silk, etc.) as raw materials, and converts carbon and hydrogen elements in raw materials into high calorific value combustible gases such as hydrogen, methane, ethane and carbon monoxide by pyrolysis. Carbon and by-products such as wood vinegar and tar are produced at the same time. The resulting carbon is clean and pollution-free. The equipment project has far-reaching significance in the development and application of waste residues recycling. The reaction mechanism is as follows: controllable reduction reaction of raw materials under anoxic condition in sealed container is carried out. The reaction process is as follows:

The first step is to dehydrate and remove the internal water.



The second step is demethylation. The reaction temperature can start at 250°C and exothermic reaction begins at 280°C.

The third step is to pyrolysis, dehydrogenation, condensation and hydrogenation of aromatic compounds generated in the previous process (about 450°C).

After the above reactions, the carbon, hydrogen and oxygen elements in the raw materials are converted into mixed combustible gases such as hydrogen, methane and carbon monoxide. These reactions have no obvious stages, and many reactions are carried out crosswise. The combustible gas is purified and transported to the burner through a pipeline to heat the carbonization furnace. At the same time, by-products such as tar and wood vinegar are separated. The whole production process is pollution-free, highly environmentally friendly, and meets the national environmental protection requirements.

This equipment adopts inner and outer double-layer cylinder, outer deep heating, heating zone using 310S stainless steel, inner heating with waste heat, used for pre-drying treatment, the whole machine adopts double-return heating structure, users are highly praised for their use.

The heat utilization rate of this equipment is higher, the material is not in contact with flue gas, and is not polluted by hot air. Compared with the single-layer external heating structure, the heat utilization rate is more than doubled. The thermal efficiency of the equipment is 70%~90%. It has good energy-saving effect. It has abundant configuration and wide application range. It is convenient and reliable to install, low installation cost for users, simple operation, safety and reliability.” (BESTON (HENAN) MACHINERY CO., n.d.).

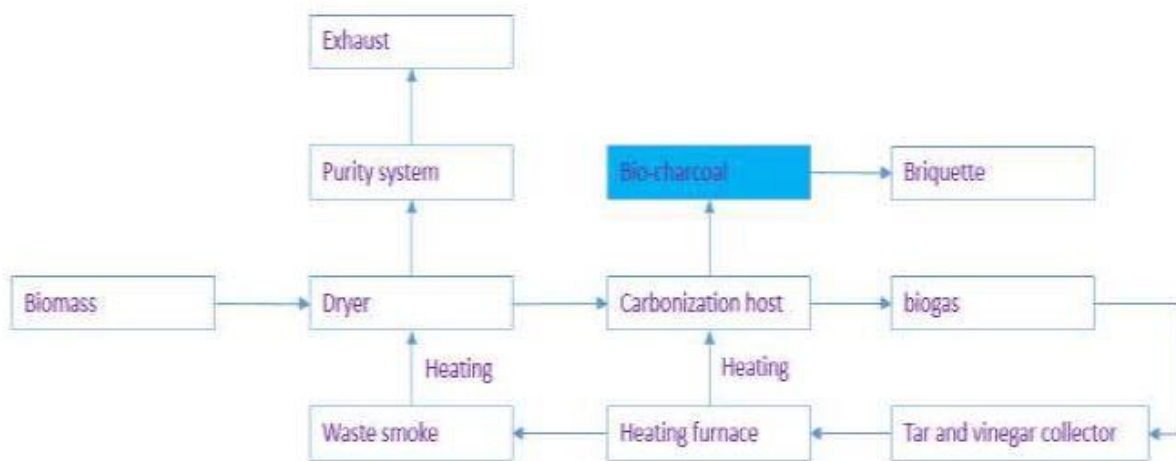


Figure 27: BESTON operation process flow diagram (BESTON (HENAN) MACHINERY CO., n.d.).



Figure 28: BESTON EQUIPMENT 3D LAYOUT (BESTON (HENAN) MACHINERY CO., n.d.).

The technical specifications provided by the supplier are represented in Table 26.

Table 26: Technical features of Beston pyrolysis equipment (BESTON (HENAN) MACHINERY CO., n.d.).

ITEM	CONTENTS
Raw material	Cocoa shells
24hrs-capacity (input)	1000 kg/h input capacity
Operating Temperature	380-500°C
Carbonization time	15-20 minutes
Workers	2-3 people/shift
Land Area	L*W*H= 45* 15*7 m
Power consumption	55kW
Water consumption	0,8- 1,5 m3
Fuel consumption	Diesel 60-80 L/hour

To compute this LCA it was necessary to introduce some assumptions: first, the yield and the quality of the products obtained are the same of the main scenario; second, the method for the assessment of the CO<sub>2</sub> emissions is the same of the main scenario.

#### 4.6.2 RESULTS

Table 27: Calculation of Estored, BESTON configuration

	$Q_{biochar}$	$C_{org}$	$H$	$H/C_{org}$	$c$	$m$	$F_p^{TH, Ts}$	$E_{stored}$
<b>Biochar (10°C)</b>	<b>dry tons</b>	<b>%</b>	<b>%</b>	<b>mol/mol</b>			<b>%</b>	<b>Ton CO<sub>2</sub></b>
<b>Cocoa shell</b>	<b>1</b>	<b>86,1%</b>	<b>1,7%</b>	<b>0,2</b>	<b>1,10</b>	<b>-0,59</b>	<b>96,4%</b>	<b>3,04</b>

Table 28: Calculation of Ebiomass, BESTON configuration.

<b>LCI System Inputs and Outputs</b>	<b>Data</b>	<b>Unit</b>	<b>Info</b>	<b>Data</b>	<b>Units per ton biochar</b>	<b>Data</b>	<b>Units per ton biochar</b>	<b>E Biomass</b>
Cocoa shells	24,0	tons per day		<b>2,6</b>	tons			
Truck	1,00	Km	Treated on site	<b>2564</b>	kgkm	<b>0,5</b>	<b>kg CO<sub>2</sub>-eq</b>	<b>0,00048</b>
Cocoa shells biochar	9,36	tons per day		<b>1,0</b>	tons			

Table 29: Calculation of Eproduction, BESTON configuration.

			<b>Study Data</b>			<b>Converted Data</b>		<b>Data</b>	<b>Units per ton biochar</b>
<b>LCI System Inputs and Outputs</b>			<b>Data</b>	<b>Unit</b>	<b>Info</b>	<b>Data</b>	<b>Units per ton biochar</b>		
<b>LCI Inputs</b>	Feedstock	Biowaste	<b>24,00</b>	tons per day		<b>2,6</b>	tons		
	Energy	Diesel	1920	L per day		<b>205,1</b>	L	<b>160,4</b>	

	Packaging		47,74	kg per day	35" x 35" x 60" bag, 55 cu. ft; weighs 2.55 kg each	5,1	kg	11,6	
	Energy	Energy Supply	1320,0	kWh per day		141,0	kWh	3,5	
		Material supply: Water	36000	kg per day		3846,2	kg		
<b>LCI Outputs</b>	Direct Air Emissions	CO <sub>2</sub> emissions	-	kg per day	Biogenic	-	kg	-	
	Biochar	Biochar	9,36	tons		1,0	tons		
<b>TOTAL</b>								175,6	kgCO <sub>2</sub> eq for production stage
<b>E production</b>								0,18	ton CO <sub>2</sub> -eq. for 1 ton of Biochar

Table 30: Calculation Euse, BESTON configuration

LCI System Inputs and Outputs			Data	Unit	Info	Data	Units per ton biochar	Data	Units per ton biochar
<b>LCI Inputs</b>	Biochar	Biochar	9,4	tons per day		1	Tons		
	Transportation	Truck	100	km		100000	Kgkm	19	kg CO <sub>2</sub> -eq
	Packaging Disposal	Super Sacks	48	kg per day		5	Kg	8	kg CO <sub>2</sub> -eq

<b>GWP, Use</b>	<b>27</b>	<b>kgCO<sub>2</sub> eq utilization</b>
<b>Euse</b>	<b>0,03</b>	<b>ton CO<sub>2</sub>-eq.</b>

		<b>CORCS</b>	E stored	E biomass	E production	E use
10 °C	<b>Cocoa shells (BESTON)</b>	<b>2,84</b>	3,04	0,0005	0,18	0,03

*Table 31: Calculation of CORCS, BESTON configuration.*

The preliminary LCA performed based on the BESTON technology results in a smaller CORC, corresponding to 2,84 ton of CO<sub>2</sub>- equivalent per ton of biochar as opposed to 2,98 ton of CO<sub>2</sub>- equivalent per ton of biochar of the PyroH technology. The main factor is the CO<sub>2</sub> associated to the production phase, where the increased requirements in term of power and the use of diesel fuel negatively affects the total net removal capability of the biochar analyzed.

## 5 CONCLUSIONS

Pyrolysis stands out as an effective method for treating heterogeneous materials like biomasses, offering significant advantages over incineration by enabling carbon capture and the production of valuable chemicals and energy. This technique supports the circular economy and aligns with the growing emphasis on carbon emission reduction and sequestration. However, challenges such as the continuous availability and handling of feedstock must be addressed to ensure process sustainability. Utilizing a continuous pyrolysis reactor emerges as a viable solution, allowing for the efficient processing of high flow rates of biomass and enhancing the overall sustainability of the operation.

Experimental activities conducted on pyrolysis of cocoa shells have reported values in line with literature, main considerations are:

- The choice of pyrolysis temperature is crucial in the definition of the quality and yield of the product
- Cocoa shell biochar is an ideal feedstock to produce biochar. It met Puro Earth eligibility criteria already at 400 °C, increasing the temperature, the H/C ratio strongly decreases, revealing the high stability (quality of this biochar).
- Biooil vapors and gases are co-products that can be combusted for energy recovery and potential energetic self-sufficiency for the entire process.
- Estored is a key parameter to identify the operating temperature. It reaches its maximum in the temperature range between 500 and 550°C, < 2% difference between the two points.
- LCA reveals that CORCs are mainly affected by Eproduction and Euse, particularly when the use of fossil fuels is requested (transport and handling).

The cocoa shell biochar applied to the soil represents an effective carbon storage technology. The preliminary LCA analysis based on the evolution of the experiment conducted with continuous feeding reveals that the cocoa shell biochar can store a quantity of carbon correspondent to 2.98 CO<sub>2</sub>-equivalent per ton of biochar. Moreover, the consistency of this result is demonstrated by the preliminary LCA based on the BESTON technology, where the CORCs generated were only 5% less.

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