



# Treball Final de Grau

**Chemical Processes Exergy Assessment in the Circular Economy**

Mariona Alcaraz López

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*Do your little bit of good where you are; it's those little bits of good put together that overwhelm the world.*

Archbishop Desmond Tutu

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## **SUMMARY**

The linear economy of taking, use and dispose of is not sustainable, and the UE is promoting the circular economy to reduce the number of resources taken from the environment and give them maximal use before being disposed of. Unfortunately, there are not many circular processes examples applied to the textile industry in the literature. The present study aims to propose a circular economy process and perform the mass balances and exergy balances. The exergy balances are a valuable tool to assess the resources consumed and lost from the assessed process. Several case studies are presented and have proven to be a viable option for the implementation of the circular economy process. However, further studies are required to minimise their environmental impact.

**Keywords:** Chemical exergy, mass and exergy balances, sustainability.



## **RESUM**

L'economia lineal d' agafar, usar i llençar no és sostenible i la Unió Europea està promovent l'economia circular per reduir el nombre de recursos que s'agafen de l'atmosfera donant-los la màxima utilització abans de ser llençats. Malauradament, no hi ha gaires exemples d'economia circular en la literatura que impliquin processos químics. L'objectiu d'aquest estudi és proposar un procés d'economia circular i aplicar els balanços de matèria i exergia. Els balanços d'exergia són una eina útil per avaluar els recursos consumits i perduts en el procés avaluat. Es presentaran diversos casos pràctics amb els seus balanços de matèria i exergia corresponents. Es realitzarà una comparació de diversos processos circulars i la seva exergia.

**Paraules clau:** Exergia química, balanços de matèria i exergia, sostenibilitat.



# 1. INTRODUCTION

Public awareness and concern about the environment have forced industries to develop and implement cleaner production processes and be more respectful towards the environment. This study focuses on a technique that will help the textile sector reduce its resource usage from the environment. It is called a circular economy (CE) and consists of reusing what was going to be thrown away. The circular economy applications are endless; this study focuses on cotton, reusing cotton fibres to produce bioplastics and turning them into fibres to produce new fabric.

## 1.1. THE TEXTILE INDUSTRY

The way we consume clothes has had a massive shift in the last 100 years. As in the past clothes were expensive, had good quality and people bought only the clothes they needed, the tendency now is to buy cheap and poor-quality clothes that have a short useful life, which leads to an increase of the quantity of post-consumer waste. The way people get rid of their unwanted clothes has also changed; most clothes are thrown out instead of donated. Globally, less than 1% of garments are recycled. (European Parliament, 2020). According to the Environmental Protection Agency (EPA), those that are not recycled end up in landfills, wherein in 2018, 7.7% of the waste was clothes.

The facts mentioned above make the textile industry considered ecologically one of the most polluting industries in the world. The issues that make the life cycles of textiles and clothing unsustainable are harmful chemicals, high consumption of water and energy, generation of large quantities of solid and gaseous wastes, massive fuel consumption for transportation, and use of non-biodegradable packaging materials (Roy, 2014).

In order to create a sustainable textile, the main change factors have been linked to eco-materials to obtain less and harmless waste, reusing/recycling, lesser usage of energy, water, and chemicals, and ethical issues in production processes. (Toprak *et al.*, 2017).

The use of bioplastics in the textile is an excellent start to make this industry a little more sustainable. Bioplastics are made from renewable sources and can be naturally recycled by biological processes, thus limiting the usage of fossil fuels and protecting the environment.

## 1.2. BIOPLASTICS IN TEXTILE

Some improvements have been made in the last few years to increase the number of bioplastics in textile production. However, 60% of textiles are still made with fossil fuels (Hahn, 2021). The biomaterials primarily used for textile are the following: polylactides (PLA), poly (hydroxy-alkanoates) (PHA), poly (hydroxybutyrate) (PHB), poly(glycolide) (PGA) and its blends, bio-polyester (bio-PES), bio-polyamide (bio-PA), thermoplastics based on casein (milk protein) and planted products: soy, kenaf, jute, silk, etc. (Grangarić *et al.*, 2013).

Some examples of bioplastics in textile in the literature are:

Rain Poncho, a product of the Spanish Company *Equilicua*, is an item of protective clothing produced from potato starch. The poncho is non-toxic, non-pollutant, and 100% compostable.



Figure 1. Rain poncho by Equilicua

(Image from [equilicua.com](http://equilicua.com))

*Kering Group*, owner of some luxury brands such as Stella McCartney, Gucci, or Yves Saint Laurent, introduced in 2012 its 5-environmental and social targets and, as a consequence, supplied these brands with APINAT Bio bioplastic in order for them to comply with the company's new policy (De Guzman, 2012). This bioplastic can be found in the soles of Stella McCartney's Fall/Winter 2012 line-up of heels and boots.



*Figure 2. Stella McCartney heels made with APINAT Bio  
(Image from Vogue.com)*

Japanese company Teijin developed a bioplastic with the name of BIOFRONT. This PLA-based and heat-resistance bioplastic has been used to create a silk crepe kimono by interweaving the BIOFRONT fibres with silk fibres to produce a new material (Thielen, 2010).



*Figure 3. Kimono silk crepe fabric  
(Image from expo2010china.hu)*

The examples shown above are some of the vast numbers of cases where bioplastics are used in textile. The primary issue that they are facing is the production cost. Currently, the bioplastic production cost is one of the significant factors that determine the effectiveness of their implementation. It is expected that bioplastics will become cheaper, mainly due to the development of new technologies and by achieving the required economy (Grangarić *et al.*, 2013).

### 1.3. CIRCULAR ECONOMY

The Circular economy's central aspect is to emphasize the materials recycling system and find the balance between economic and environmental development with the use of available resources. CE assumes that each waste stream should become a product (or a secondary raw material) (Ragossnig and Schenider, 2019).

Gradually, the CE wants to substitute the linear economy pattern of "take → make → waste" because human society, for a long time, has been consuming resources at a higher rate than the environment can replenish (Fan *et al.*, 2021).

There are many circularity studies in the literature about metals, plastics (Klemeš *et al.*, 2021), wood, construction (Anastasiades *et al.*, 2020). However, not a lot for the textile/fashion industry.

The Ellen Mc Arthur Foundation (2021) established the three principles of the CE as designing out waste and pollution, keeping products and materials in use, and regenerating natural systems. Applying these principles to the textile industry would be new business models that increase clothing use, safe and renewable inputs, and solutions so used clothes are turned into new ones.

A great example of the circular economy applied to the fashion industry is the brand Patagonia. They launched a program named "Worn Wear" (2017), through which the customers are given the possibility to repair their clothes and equipment of quality that has already been used rather than buy them new. They also offer a service for trading in old clothes in exchange for store credit. This program and other initiatives made the brand win the "Circular Economic Multinational Award" at World Economic Forum 2017 (Byars, 2017).



## 1.4. COTTON

Cotton is one of the most used materials for textiles, accounting for about 33% of all fibres found in textiles (Drew *et al.*, 2017). It is considered a natural fibre because it is derived from a plant (Chand *et al.*, 2021). Principally used in shirts, pants, and underwear, this material is lightweight yet resistant. Its main advantage is that it can be recycled without using chemical additives (Ellen McArthur Foundation, 2017).

Cotton fibres consist essentially of 95% cellulose; the remaining 5% compounds are located primarily in the cuticle and primary cell wall and contain wax, pectic substances, organic acids, sugars, and ash-producing organic salts. After chemical processing, these noncellulosic materials are removed, and the cellulose content of the cotton fibres increases to more than 99% (Chand *et al.*, 2021).

Cellulose is the result of the union of glucose molecules by  $\beta$ -glycosidic bonds. The number of glucose molecules in the chain depends on the precedence and state of the cellulose fibre. Figure 4 shows the general formula of cellulose.

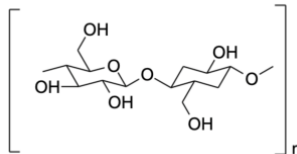


Figure 4. Cellulose

The following list of cotton fibre properties was obtained from Potter *et al.* (1954).

- Easily spurned into yarns due to the natural twist of cotton fibres.
- Elasticity: Cotton has no elasticity, so cotton fibres are easily wrinkled.
- Good conductors of heat make cotton fibres suitable for summer clothing
- Absorb water quickly; therefore, it does not dry well
- Soils easily. Considered a hygienic material because it can be cleaned easily it withstands rough handling and boiling temperature.

- Resistant to degradation by heat. Scorches at about 150 °C but does not burn until the temperature is 247 °C.
- Damages easily by acids but not injured by alkalis.

## 1.5. POLYHYDROXYALKANOATES (PHAs)

Polyhydroxyalkanoates (PHAs), also known as poly (3-hydroxyalkanoates), are biopolyesters synthesized intracellularly by some microorganisms. These microorganisms use PHA as their carbon and energy storage and, at specific conditions and if extracted from the microbial cell, they present physical properties that are similar to petroleum obtained plastics. They are of growing interest in the industrial sector for being precursors of biocompatible and biodegradable plastics (González García *et al*, 2013).

Chemically they are defined as hydroxy alkanic acids that some microorganisms accumulate intercellularly as reserve material. The polymerization of hydroxy alkanic acids, by the action of intercell enzymes, occurs by condensation of the carboxyl group of a monomer (hydroxy alkanic acid) with a hydroxyl group forming an ester bond. Hence, they are known as biopolyesters. (Khanna and Srivastava, 2005). Figure 5 shows the general formula of PHAs.

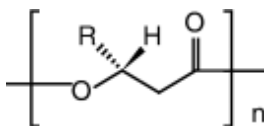


Figure 5. Poly(3-hydroxyalkanoates)

(Image from Verlinden *et. al.*, 2007)

The n value depends on the group R and the microorganism in which the biopolymer is produced, taking values between 100 and 30,000 (Lee, 1996). Table 1 contains those that are the most common substitutions of the radical group and the names the polymer receives (Andler and Díaz, 2013).

Table 1. Most common PHAs

R group	Polymer Name	Abbreviation
CH <sub>3</sub>	Poly(3-hydroxybutyrate)	PHB
CH <sub>2</sub> CH <sub>3</sub>	Poly(3-hydroxyvalerate)	PHV
CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Poly(3-hydroxyhexanoate)	PHHx

(Source: Andler and Díaz, 2013)

Depending on the carbon numbers in the monomeric constituents, PHAs can be classified as short-chain-length PHAs (SCL-PHA, C<sub>3</sub>-C<sub>5</sub>), consisting of 3-5 carbon monomers medium-chain-length PHAs (MCL-PHA, C<sub>6</sub>-C<sub>14</sub>). For example, PHB, PHV, and their copolymer PHBV are typical examples of SCL-PHAs, whereas PHHx is a typical example of MCL-PHA. More than 150 different PHA monomers have been identified, making them the largest group of natural polyesters (Li *et al.*, 2016).

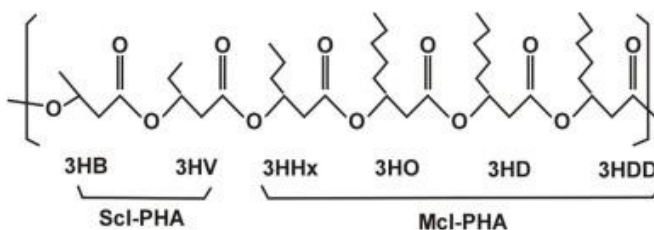


Figure 6. General molecular structure of PHAs

(Image from Ali Raza *et al.*, 2018)

The chemical properties of this bioplastic can vary. Molecular weight depends on the conditions of production and recovery (Verlinden *et al.*, 2007). The kind of microorganism and the carbon source influence the molecular weight obtained, as does the extraction solvent used. Organic solvents lead to polymers with higher molecular weight than the extraction with sodium hypochlorite or other chemicals (Alcaraz, 2015).

Even though PHAs present important environmental advantages compared with petrochemical plastics, the major issue regarding the production of this biopolymer is its high

cost (Andler and Díaz, 2013), which is why some measures are being taken to make them more accessible to the common population. Those measures include improvements in the fermentation and extraction processes.

PHA can be produced by one single microorganism (pure culture) or a consortium of microorganisms (mixed culture). However, its economic production will depend not only on the costs of the raw material of coal but also on the aseptic conditions of the cultivation (monocultures) that are the most used technology or production by mixed microbial cultures (MMCs) (Dai *et al.*, 2007).

The production of PHA using MMCs offers an advantage compared to pure culture, being that in this type of fermentation, sterile conditions are not necessary (Arcos, 2007). In either case, establishing the optimal values for each operating parameter is needed, being temperature, pH, and fermentation time those with the highest incidence (Kulpreecha *et al.*, 2009). However, the major challenge is designing a bioprocess with a high conversion efficiency at the lowest cost (Andler and Díaz, 2013).

### 1.5.1. PHA Production

PHA production is a survival mechanism that some microorganisms develop to face a shortage of substrate and nutrients. In those circumstances, which can be phosphorous, nitrogen or oxygen limitation, non-optimal pH, or an excess of carbon source, PHA is accumulated intracellularly as an energy reservoir. Studies have demonstrated that bacteria can reach a 90% of their weight in PHA molecules (Madison and Huisman, 1999).

When accumulated, PHAs are liquid, mobile, and amorphous polymers in the form of granules located in the cytoplasm surrounded by a phospholipid monolayer, shown in Figure 2 containing polymerases depolymerizes enzymes (Ábalos *et al.*, 2003; Gómez, 2013). The number of granules per cell is defined in the early stages of the process, and polymer production ceases when the accumulation content reaches between 80-90% of cellular dry mass (Cantone, 2013).

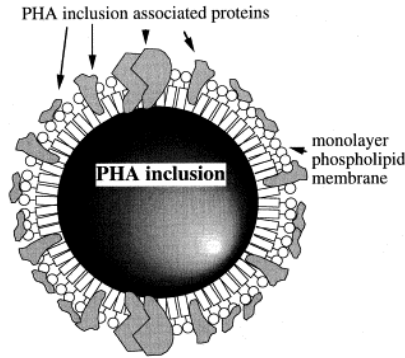


Figure 7. PHA granule

(Image from Sudesh et. al., 2000)

The efficiency in the PHA production process strongly depends on culture selection by the conditions imposed on the bioreactor; Feast and Famine (FF) regime is used to achieve the goal (Alcaraz, 2015). Mixed microbial culture (MMC) PHA production processes are usually being carried in three sequential stages: acidogenic fermentation, culture selection, and PHA accumulation (Reis et al., 2011).

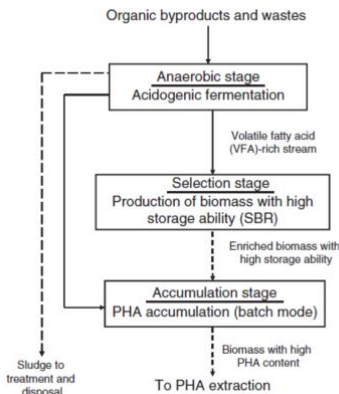


Figure 3. Three-stage sequential production process of PHA using Feast and Famine Sequencing Batch Reactor (SBR)

(Image from Reis et. al., 2011)

The production process does not end here because PHA has to be extracted from inside the cells. Extraction is done by solubilizing the intracellular PHA, followed by separation of the extracted residual biomass and isolation of PHA from the solvent (de Souza *et al.*, 2020). Chlorinated solvents, such as chloroform and dichloromethane, are considered reference solvents for their high efficiency. However, non-halogenated solvents have sometimes been used in literature and, even though their efficiency is not as high, they are characterized by their low toxicity.

### 1.5.2. PHA Biodegradability

One of the essential characteristics of PHA is its biodegradability. Microorganisms in nature can degrade PHAs by using the enzymes PHA hydrolases and PHA depolymerase. These degrade the PHA into carbon dioxide or methane and can work in either anaerobic or aerobic conditions. Even though the degradation rate is not easily predicted, some studies have shown that higher temperatures lead to better degradation, which is probably due to an increase in microbial activity (González-García *et al.*, 2013).

There are some polymer parameters that affect the degradation rate, which are the monomeric composition of the polymer, crystallinity or amorphous regions (higher crystallinity leads to lower degradation), and molecular weight (low molecular weight polymers lead to higher degradation). Microorganisms colonize the surface of polymers, secreting depolymerases which hydrolyse the ester bond of the PHA producing oligomers, dimers that are subsequently taken to their monomeric forms such as poly (3- hydroxybutyrate) to hydroxybutyrate or poly (3- hydroxy valerate) to hydroxy valerate (Alcaraz, 2015).

PHAs are fully biodegradable to carbon dioxide and water under aerobic conditions and methane under anaerobic conditions. The carbon dioxide released as the final mineralization product of biopolymers is used as the renewable carbon source for their biosynthesis. Photosynthetic fixation of the released carbon dioxide by plants generates renewable carbon sources again. Thus, the carbon flux in the synthesis and degradation of biopolymers is balanced. Therefore, PHAs do not contribute to global warming.

### 1.5.3. PHA Fibres

PHAs have poor mechanical properties if found alone. However, they can be modified to ensure improved performance in specific applications. PHAs have been compared to polypropylene (PP) for their similar properties in terms of offering good resistance to moisture and aroma barrier properties (Bugnicourt *et al.*,2014).

The blending of PHA with other polymeric or natural raw materials has also been considered an excellent way to improve its properties. Cellulose derivatives have attracted a significant amount of interest as blending components with PHA primarily due to their compatibility with PHA and their ability to enhance the degradation of PHA. (Li *et al.*, 2016).

PHA properties include good ultraviolet resistance, non-toxicity, water insolubility, and poor resistance to both acids and bases (Bugnicourt *et al.*,2014).

## 1.6. POLY LACTIC ACID (PLA)

Poly (lactic acid) (PLA) is an aliphatic polyester whose precursor molecule is lactic acid (LA). It can also be categorized as thermoplastic, biopolymer, and biodegradable. Due to its biodegradability, barrier properties, and biocompatibility, this biopolymer has numerous applications since it has an extensive range of properties that can be achieved by manipulating mixtures between D (-) and L (+) isomers, molecular weights, and copolymerization (Bello, 2004). Generally, commercial PLA is a copolymer between poly (L-lactic acid) and poly (D-lactic acid) with a higher content of poly (L-lactic acid) (Auras *et al.*, 2010). Figure 8 shows the general formula of PLA.

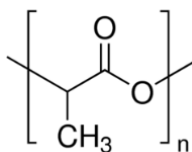


Figure 8. Poly(lactic acid)

(Image from Sigma Aldrich, 2019)

It is produced by the polymerization of lactic acid, and this can be obtained by anaerobic fermentation of carbohydrates or by chemical synthesis.

Most fermentation processes today use a gen of lactobacilli that produces a high rate of lactic acid. The general processing conditions of this bacteria include a pH of 5.4 – 6.4, a temperature of 38 – 42 °C, and a low oxygen concentration. Currently, the most widely used is *Lactobacillus delbrueckii* (Serna *et al.*, 2003).

If produced by chemical synthesis, acid lactic is obtained by the reaction of acetaldehyde with hydrocyanic acid to give lactonitrile, which can be hydrolysed to lactic acid. Another type of reaction is the high-pressure reaction of acetaldehyde with carbon monoxide and water using sulfuric acid as a catalyst (Auras *et al.*, 2010).

### 1.6.1. PLA Production

Polymerization of lactic acid can be carried out by three different methods: direct condensation polymerization, azeotropic dehydrating condensation, and ring-opening polymerization (ROP) through lactide formation (Auras *et al.*, 2010).

In direct condensation polymerization, acid lactic can be polymerized by condensation due to hydroxyl and carbonyl groups. Even though this is the most economical and straightforward way to polymerize lactic acid, the PLA obtained has a low molecular weight, and the use of coupling agents is required to increase its molecular weight while increasing its economic costs.

By azeotropic condensation high molecular weight, PLA can be obtained without the use of coupling agents. High quantities of catalyst are applied to increase the reaction rate, but the catalyst residues can cause unwanted degradation, uncontrolled rates, or toxicity.

The ROP process is based on removing water under milder conditions, without solvent, to produce a cyclic intermediate dimer, referred to as lactide. ROP polymerization of the dimer is accomplished under heat. By controlling the purity of the dimer, it is possible to produce a wide range of molecular weights (Farrington *et al.*, 2005).



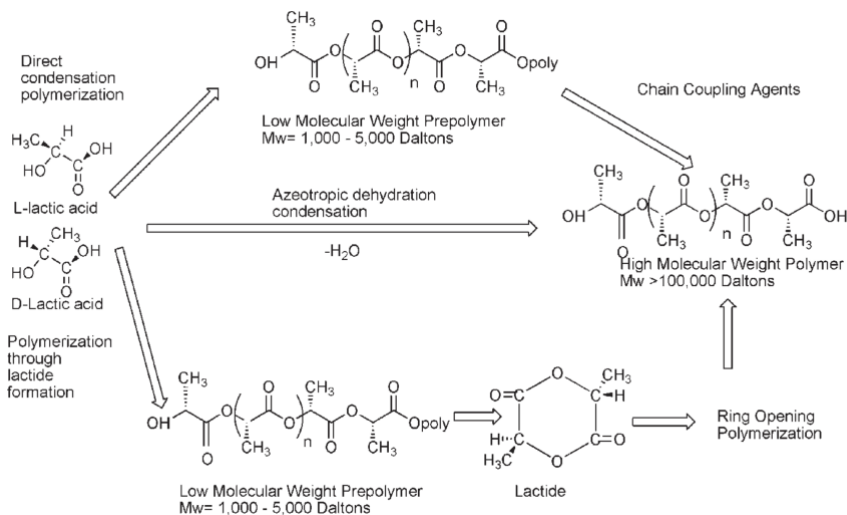


Figure 9. Synthesis methods for obtaining high molecular weight PLA

(Image from Auras *et al.*, 2004)

### 1.6.2. PLA Biodegradability

The degradation of PLA has been under study several times, but nothing has been firmly concluded. There is not sufficient information on the mechanisms involved and microorganisms associated with the PLA degradation. Some reports state that PLA degradation occurs only through hydrolysis without enzymatic involvement (Pranamuda *et al.*, 2001). Others suggest that enzymes have a significant role in the degradation of PLA (Nakamura *et al.*, 2001).

Generally, polymer degradation takes place through the scission of the main chains or side chains of polymers. However, some factors that affect the biodegradability of polymers in general also apply to PLA. These are the molecular weight, crystallinity (See 1.5.2), and melting temperature (the higher melting point, the lower biodegradability tends to be) (Towika *et al.*, 1979).

Li *et al.*, (1999) studied the effects of the stereoisomeric content of PLA on the degradation rate of PLA and concluded that the degradation rate increased with the high content of L-lactic acid monomers.

The biodegradability of PLA depends on the environment to which it is exposed. They can be degraded in a composting environment where they are hydrolysed into smaller molecules (oligomers, dimers, and monomers) after 45-60 days at 50-60°C. These smaller molecules are then degraded into CO<sub>2</sub> and H<sub>2</sub>O by microorganisms in the compost (Tokiwa & Calabia., 2006).

### 1.6.3. PLA Fibres

PLA fibres have many properties studied by several researchers, and these have concluded that PLA has significant commercial potential as textile fibre (Farrington *et al.*, 2005). Its mechanical properties are considered to be broadly similar to conventional Polyethylene Terephthalate (PET) (Lunt *et al.*, 2001). Some of its properties, such as controlled crimp, smooth surface, and low moisture regain, are thermoplastic characteristics.

PLA can achieve a good retention level through processing; both filament and spun yarns can be made, as with PET. It also has a high limit oxygen index (LOI) compared to most fibres, which means it is more difficult to ignite.

A test by Odor Science and Engineering (2005) showed that PLA fibres outperformed PET-fibres for low odor retention. PLA resistance to hydrolysis is poor due to being a linear aliphatic fibre. It also has limited solubility and therefore is not affected by dry-cleaning solvents.



Figure 10. PLA Fibers

(Image from [mktmakeit.com](http://mktmakeit.com))

## 1.7. POLYETHYLENE

Polyethylene (PE) is a thermoplastic with a variable crystalline structure. PE has the simplest basic structure of any polymer (it is a repetition of CH<sub>2</sub> units, see Figure 11). However, it is the worldwide most produced plastic. Some of its more attractive features are its low price, excellent chemical resistance, good processability, and flexibility (Ronca, 2017).

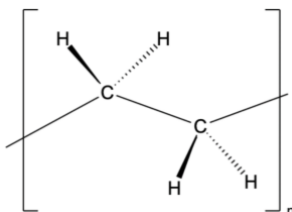


Figure 11. Polyethylene

Various industrial processes exist for obtaining PE, depending on the properties to be obtained in the final product, giving rise to different types of PE. Depending on the polymerization conditions, polymers with different branches are obtained, affecting their density and crystallinity. Because of this, PE is generally classified by its density (Ehreenstein, 2007). Low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) are the most used.

PE fibres feel soft and silky and can be engineered to feel like cotton. In addition, PE fibres can be weaved into textiles by an extrusion process that makes the PE on the surface of the fibres oxidize, giving it moisture-wicking properties. Because the inside of the fibres is hydrophobic, the moisture does not seep in but instead evaporates quickly. (Alberghini *et al.*, 2021).



Figure 12. Polyethylene fibers

(Image from Imteaz, 2016)

Even though PE is a non-biodegradable polymer, it is one of the most accessible polymers to be recycled. Chemical recycling is the most efficient. It consists of chemically converting the polymers into monomers or partially depolymerizing them into oligomers through a chemical reaction. The resulted monomers can be used for new polymerizations (Grigore, 2017).

## 2. OBJECTIVES

The aim of this work is to determine if it is possible to create, by means of a bibliographical search, a viable process for the circular economy of cotton by degrading cotton fibres into PHA and PLA. When this is achieved, an exergy balance will be performed for each process and a critical comparison of both. Also, a comparison to the same process obtaining polyethylene (PE) that was carried by Plesu *et al.* (2021) is going to be assessed.

### 3. METHOD

In this section, the method that was followed during this study is provided, allowing those interested in applying it.

The first step is to choose the polymer that is going to be produced from the cotton waste. There exist many polymers in literature. Note that choosing a biodegradable polymer would be less prejudicial to the environment, thus contributing to the aim of the circular economy.

The second step is to define the principal materials and products. These include the primary materials, intermediate products, by-products, and final products involved. This step is based on a bibliographical search.

The third step is the identification of all streams in the process and their temperature and pressure conditions. A process flowchart can be included in this step but is not required.

The third step is to solve the overall mass balances using a calculation basis. Microsoft Excel allows for this calculation.

The fourth step is to solve the exergy balances. The physical exergy of each stream is done in referral to that same stream at the reference conditions, which are 25°C and 1 bar, and using the mass flows. The commercial simulator Aspen Plus® allows for this calculation. Chemical exergy can be done by bibliographical search and using an online tool named Eco exergy Calculator (Valero and Valero, 2018) that requires Gibbs energy for each component. For the materials whose chemical exergy cannot be calculated by the online tool, such as biomass or MMC, an equation adapted from Eboh *et al.* (2016) (Eq. 1) can be used. This equation is a function of its heating value dependent on the weight percentage of each sort of atom in the mixture (Plesu *et al.*, 2021).

$$EX = 376.461 \times C + 791.018 \times H - 57.819 \times O + 45.473 \times N - 1536.24 \times S + 100.981 \times Cl \quad (1)$$

The fifth step is the identification of the assets and liabilities. Assets correspond to residual streams to the environment, while liabilities correspond to resources consumed from the environment.

The last step is the proposal of ideas to minimize the calculated exergy.

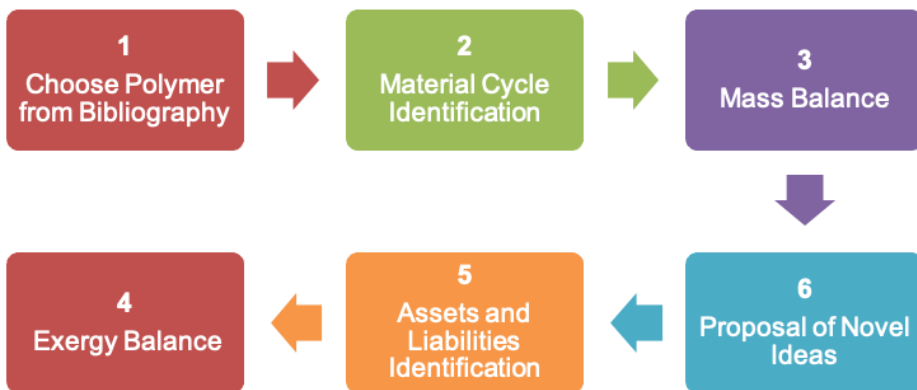


Figure 13. Steps for the exergy assessment





## 4. RESULTS

In the below section are shown the result processes, mass and exergy balances of the cases studies of this work. These processes have been carried out by means of a bibliographical search.

### 4.1. PHA

#### 4.1.1. Process

Figure 14 shows the circular process scheme considered in this study. Considering cotton as the raw material, it will undergo an acidogenic fermentation to produce volatile fatty acids. An acidogenic fermentation done with a substrate-to-inoculum ratio (SIR) of 0.5 allows for an anaerobic degradability of 89.67% (Juanga-Labayen *et al.*, 2021). The VFAs obtained will be taken into an Aerobic reactor where a MMC is to be found for the Feast and Famine process.

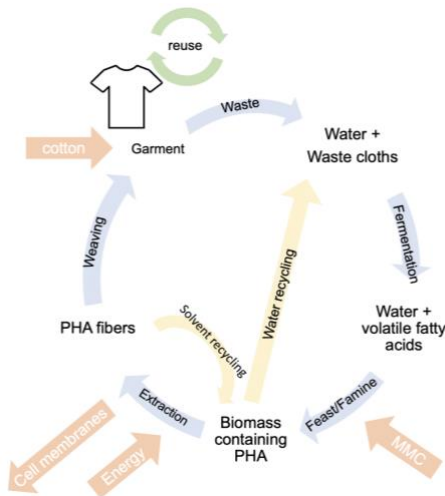


Figure 14. Circular process scheme

After Feast and Famine, a current of biomass containing PHA is obtained, which has to go through a reflux extraction process using dimethyl carbonate (DMC) as a solvent (de Souza *et al.*, 2020). There are other chlorinated solvents in the literature that have shown more efficiency, such as chloroform and dichloromethane (Manangan *et al.*, 2010). However, being one of the circular economy aims to minimize environmental damage, dimethyl carbonate has been chosen for this study due to its low toxicity, a characteristic that makes DMC a green solvent.

A next step of purification of the PHA with 1-butanol is possible but considering the purity obtained of the PHA is 91.2% (de Souza *et al.*, 2020), it has been considered non-necessary.

When PHA is obtained, the PHA fibres are combined with cotton fibres to produce new clothes. When these clothes reach their useful life, they will be considered raw materials for the process, closing the cycle.

#### 4.1.2. Mass Balance

Figure 15 shows the process flow diagram from which the mass balance has been made. Drawing has been made using the design software *AutoCAD*. This balance has been made by taking the input/output streams to/from the cycle and using a calculation basis of 1kg of cotton. Using that basis, 243g of PHA are produced, which then are added to the input stream from the environment reducing the amount of cotton that has to be taken from 1000g to 757g.

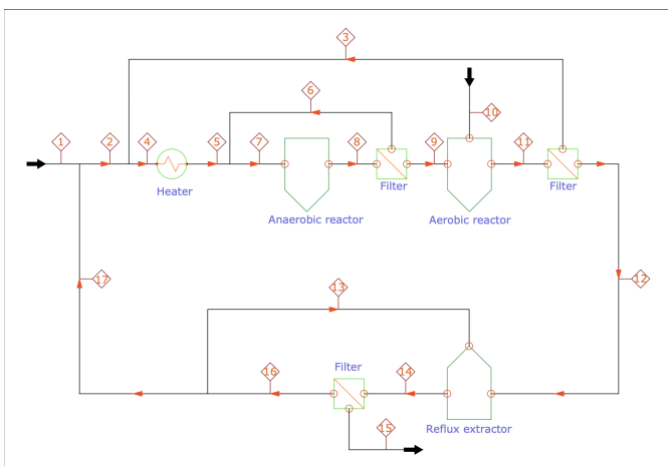


Figure 15. Process flowchart

The conversion of cotton to PHA is 0.22g PHA/ g substrate (Basset *et. al*, 2016), which by recirculating the cotton that has not been degraded, reaches 0.24g PHA/g substrate.

Stream 1 (S1) comes from the environment, which is the stream with the raw material, cotton. Stream 2 (S2) is the union between S1 and Stream 17 and adds the PHA obtained to the cotton. A stream of water, Stream 3, is added to S2, creating Stream 4. In S4, raw materials enter at ambient temperature and have to go through a heater to reach a temperature of 35°C, so that mesophilic conditions are achieved, they come out heated as Stream 5 (S5). To S5, a stream containing cotton and PHA that has not been degraded, Stream 6 (S6), is added, resulting in Stream 7 (S7). S7 enters an Anaerobic Reactor in which fermentation is carried. What comes out of the reactor is Stream 8 (S8) and contains VFAs and the raw material that has not been degraded.

The VFAs are obtained in a concentration of 11.53 g/L, and the proportion showed in Table 2 as obtained experimentally by Cheah *et al.* (2019).

Table 2. VFAs proportion after Acidogenic Fermentation

VFA	Percentage
Acetic acid	35.27 %
Propionic acid	22.05 %
Butyric acid	19.79 %
Valeric acid	11.60 %
Other acids	11.29 %

(Source: Cheah *et al.*, 2019)

Next, there is a filter to recirculate the cotton and PHA that has not been degraded. Cotton recirculates through Stream 6. VFAs and water stay in Stream 9 and enter an Aerobic reactor

where a Feast and Famine process occurs, and microbial cells accumulate PHA. Stream 10 is an input of MMC that enters directly into the reactor. Stream 11 is a current of water and biomass containing PHA, which has to be extracted. First, it is filtered to separate the water from the solid material, obtaining a Stream 12 with only biomass containing PHA. The extraction is done by solubilizing the intracellular PHA and then separating the extracted residual biomass using a filter. Separation of the PHA from the solvent is carried by evaporating the solvent, DMC, which has a boiling point of 90°C. Stream 13 is used for the recirculation of DMC. In Stream 14, the PHA is solubilized in the DMC. Next, a filter is used for separating the cell membranes, which go to the environment as an output. In Stream 16, the DMC is evaporated and recirculated, and PHA on its own is obtained in Stream 17, thus closing the cycle.

The quantity of solvent used is calculated using a solvent ratio of 1%, which leads to approximately an obtention of 30.7 g PHA/g biomass as calculated by de Souza et. al. (2020). The solvent is considered totally recovered, for there is no need to have an inflow.

Table 3 and Table 4 correspond to the mass balance of the process and have been solved with Microsoft Excel.

Table 3. Mass balance

	Streams							
	1	2	3	4	5	6	7	8
<b>Temperature (°C)</b>	25	25	25	25	35	35	35	35
<b>Pressure (bar)</b>	1	1	1	1	1	1	1	1
	<b>Mass flow (g/h)</b>							
cotton	757							
cotton + PHA		1000		1000	1000	114	1103	114
H2O			22358	22358	22358		22358	22358
Acetic acid								87
Propionic acid								54
Butyric acid								49
Valeric acid								29
Others VFAs								28
MMC								
Biomass containing PHA								
Dimethyl Carbonate								
Cell membranes								
PHA								
<b>Total</b>	<b>757</b>	<b>1000</b>	<b>22358</b>	<b>23358</b>	<b>23358</b>	<b>114</b>	<b>23462</b>	<b>22719</b>

Table 4. Mass balance

	Streams								
	9	10	11	12	13	14	15	16	17
<b>Temperature (°C)</b>	35	25	25	25	90	90	25	90	25
<b>Pressure (bar)</b>	1	1	1	1	1	1	1	1	1
	<b>Mass flow (g/h)</b>								
cotton									
cotton + PHA									
H <sub>2</sub> O	22358		22358						
Acetic acid	87								
Propionic acid	54								
Butyric acid	49								
Valeric acid	29								
Others VFAs	28								
MMC		243							
Biomass containing PHA			791	791					
Dimethyl Carbonate					84836	84836		84836	
Cell membranes						548	548		
PHA						243		243	243
<b>Total</b>	22605	243	23149	791	84836	85627	548	85079	243

### 4.1.3. Exergy Balance

An exergy assessment is performed overall case study to determine where the leading share of resource losses impacts the environment. Table 5 and Table 6 present the exergy values, both chemical and physical, for each stream. For chemical exergy values of all components see *Appendix 1*.

Physical exergy has been obtained by a simulation with Aspen Plus®. The reference conditions are set to be at 25°C and 1 bar. Below in Table 5 and Table 6, the exergy flows in referral to 1 kg of PHA produced are presented.

Table 5. Exergy balance

	Streams							
	1	2	3	4	5	6	7	8
<b>Temperature (°C)</b>	25	25	25	25	35	35	35	35
<b>Pressure (bar)</b>	1	1	1	1	1	1	1	1
<b>Physical Exergy (kJ/kg PHA)</b>	0	0	0	0	7892	-44	7851	8290
<b>Chemical Exergy (kJ/kg PHA)</b>	86978	114857	10821	125678	125678	13090	137543	86478
<b>Total Exergy (kJ/kg PHA)</b>	86978	114857	10821	125678	133570	13047	145394	94768

Table 6. Exergy balance

	Streams								
	9	10	11	12	13	14	15	16	17
<b>Temperature (°C)</b>	35	25	25	25	90	90	25	90	25
<b>Pressure (bar)</b>	1	1	1	1	1	1	1	1	1
<b>Physical Exergy (kJ/kg PHA)</b>	8336	0	0	0	121825	120769	0	122971	0
<b>Chemical Exergy (kJ/kg PHA)</b>	7338 7	2074 1	24839 3	23757 2	163314 36	165742 40	16463 7	164096 03	7816 7
<b>Total Exergy (kJ/kg PHA)</b>	8172 3	2074 1	24839 3	23757 2	164532 61	166950 09	16463 7	165325 74	7816 7

The next step is the identification of the assets and the liabilities. Only the input and output streams from the cycle are considered in the assessment as the internal streams have no impact on the environment. The exergy requirements for obtaining raw cotton constitute a significant fraction of the liabilities, while the PHA extraction provides the main contribution (asset) in reducing the exergy footprint.

The exergy assets are 164,64 MJ/kg PHA, and the exergy liabilities are 107,72 MJ/kg PHA. That makes an exergy footprint of 56 MJ/kg PHA.

## 4.2. PLA

### 4.2.1. Process

Figure 15 shows the circular process scheme considered in this study. Considering cotton as the raw material, it will decompose to form lactic acid.

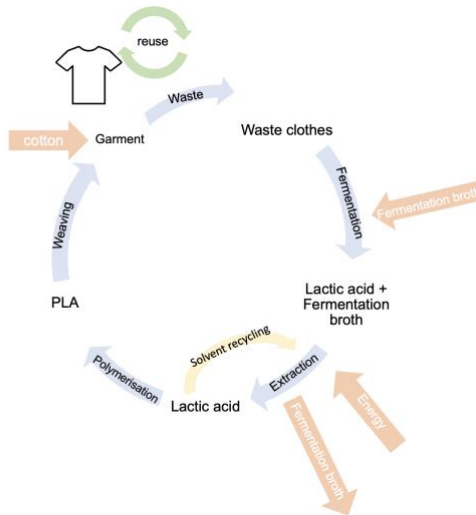


Figure 16. Circular process scheme

Cotton waste undergoes a fermentation process using as a fermentation broth a strain of *Lactobacillus delbureckii*, lactic acid producing bacterium (LAB). This fact is bearded out by Tsapekos *et al.* (2020). The feeding rate is adjusted through fed-batch fermentation to overcome end product inhibition (Othman *et al.*, 2017). Optimum pH and temperature are 6 and 37°C, respectively (Ahmad *et al.*, 2020).



Because the fermentation broth includes a complex mixture of impurities, nutrients, and cell debris, the downstream processing of lactic acid plays a decisive role in the overall production route of PLA. The detection and removal of impurities is essential because they can strongly deteriorate the properties of the produced polymer (Achmad *et al.*, 2009).

The lactic acid fermentation broth contains impurities such as organic acids, alcohols, lactates, amino acids, protein fragments deriving from the cell mass, colour bodies, residual nutrients, metabolic intermediates, and fermentation by-products (Inikinen *et al.*, 2011), and reactive extraction needs to be implemented.

In the reactive extraction, there is a reaction between extractant and material extracted. The extractant in the organic phase reacts with the material of the aqueous phase, and the reaction complex formed is solubilized into the organic phase (Han *et al.*, 2000).

First, the LA is transferred from the fermentation broth to a solvent phase and forms an acid-amine complex and a relatively acid-free aqueous raffinate. Next, the LA needs to be stripped from the organic complex to obtain amine-free aqueous lactic acid. The extractant is recycled back to the extraction unit (Udachan *et al.*, 2014).

Tri-*n*-octylamine (TOA) has been chosen as the reactive extractant for this study because its high Brønsted basicity has been reported to provide high distribution coefficients for carboxylic acids (Painer *et al.*, 2017). However, TOA has to be diluted to improve physicochemical properties. The optimized solvent phase containing 40w% TOA, 40w% 1-octanol, and 20w% *n*-undecane provides a highly efficient extraction of lactic acid (Mungma *et al.*, 2019).

Back-extraction of the LA from the solvent phase is necessary. A stripping solution containing  $\text{NaHCO}_3$  is being used as its effectiveness has been proved by Mungma *et al.* (2019).

The final step is the polymerization of lactic acid that will be carried by a process that NatureWorks LLC developed and patented (Gruber *et al.*, 1992). It is a low-cost continuous process for the production of LA-based polymers based on the ROP. This process starts with a continuous condensation reaction of aqueous lactic acid to produce a low molecular weight PLA prepolymer. The prepolymer is then converted into a mixture of lactide stereoisomers using tin catalysts to enhance the rate and selectivity of the intramolecular cyclization reaction. Molten

lactide mixture is purified by vacuum distillation. The PLA polymer is produced using a tin-catalysed, ring-opening lactide polymerization. After polymerization, remaining monomers are removed under vacuum and recycled (Farrington *et al.*, 2005).

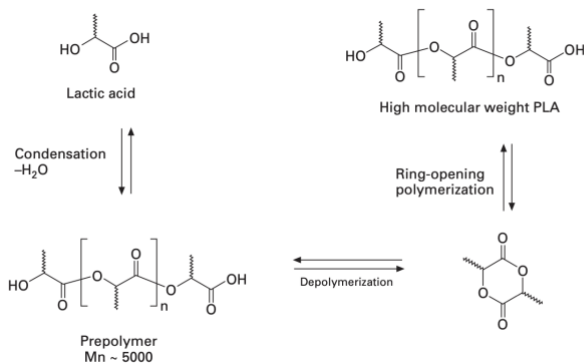


Figure 17. Production of high molecular PLA

(Image from Farrington *et al.*, 2005)

A final step is garment making from PLA fibres. Something to take into account is that the low melting point of PLA (between 150-160°C, Springer Materials) makes having to be careful at those stages where fibre-metal friction could generate enough heat to melt the fibres (Farrington *et al.*, 2005).

#### 4.2.2. Mass Balance

Mass balances could not be carried because there was insufficient data in the literature to provide stats for all phases of the process. However, the quantity of PLA produced from 1kg of cotton waste has been calculated using a reference to a study from Kim *et al.* (2003) in which the quantity of lactic acid produced from 1 kg of kitchen waste is calculated. The data extracted

from this article is “27 g/L lactic acid from 60 g/L food,” which equals 450 g lactic acid/ kg food waste.

A comparison with the production of ethanol from kitchen and cotton waste has been made to calculate this figure. Tang et al. (2008) developed and carried a process for ethanol production from kitchen waste and obtained that 30,9 g ethanol can be produced from 1 kg of kitchen waste. Plesu *et al.* (2021) calculated that 279 g of ethanol could be obtained from 1 kg of cotton waste.

Using all this data a calculation has been made to produce lactic acid from cotton waste resulting in 698 g of lactic acid from 1 kg of cotton waste.

## 5. DISCUSSION

In this section, a comparison of the circular economy of cotton processes to produce PHA, PLA, and PE will be made.

Table 7 shows the product obtained from 1 kg of cotton waste.

Table 7. Product obtained from 1kg cotton

Polymer	Quantity obtained from 1 kg of cotton
PHA	243 g
PLA	698 g
PE	170 g

PLA suggests that it would be the best option because it has the highest production efficiency and is entirely biodegradable. However, as the exergy footprint has not been obtained, there is no certainty and cannot be critically compared.

Next, in Table 8, the exergy footprint produced per kg of product for PLA and PE processes is shown.

Table 8. Exergy footprint produced for each kg product

	Assets	Liabilities	Exergy
PHA	165 MJ/kg PHA	108 MJ/kg PHA	56 MJ/kg PHA
PE	138 MJ/kg ethylene	153 MJ/kg ethylene	15 MJ/kg ethylene

The fact that liabilities are minor for the PHA process than for the PE process indicates that PHA process has less impact in the natural resources e.g., less cotton fields needed. However, assets for the PHA process are higher than for the PE process, meaning the PHA process loses more exergy towards the environment.

The only contributor to the Assets of PHA are the cell membranes sent into the environment post-filtration at a temperature of 90°C. The main contributor to the Liabilities is the cotton that has to enter the process.

Plesu et al. (2021) state in their article that the main contributor to the liabilities is the cotton raw material, and for the assets is the degradation of polyethylene.

One of the main focuses of the PHA process is to find a way to increase the production, which will mean that less cotton has to enter the process, and thus the liabilities will decrease. Therefore, the interest is in finding a method that can increase the production of VFAs from the cotton, which now is 0,22 g VFAs/g cotton.

Yin et al. (2014) studied the improvement of VFA production from food waste, which could be approximated to cotton waste, and concluded that a hydrothermal treatment of the substrate at 160°C enhanced the production of VFAs. However, adding a pre-treatment to the process could increase the energy consumption, but further study would be needed to determine if the increased production compensates for this.

To reduce the assets, which come essentially from cell membranes, a promising approach is to decompose these cell membranes and use them as a raw material for the process. Yadav *et al.* (2020) researched various methods in which these cell membranes can be recovered. Some of these include a pre-treatment of the fermentation broth before extraction and protein precipitation of the cell membrane.

## 6. CONCLUSIONS

From the results obtained throughout this work, the following general conclusions have been deduced:

The linear economy pattern currently used is no longer a viable option and needs to be substituted with a Circular Economic pattern. Significant improvements have been made in the textile industry to reduce the environmental damage that this industry has and is still causing. PHA and PLA production from cotton waste is feasible. It is possible by Chemical Recycling to produce enough fibres for mixing with cotton fibres and eliminate the need for petrol-based fibres. There are aspects of the production process for PHA that need to be worked on to reduce its exergy footprint. This study contributes to the development of an exergy footprint assessment method implementing the Circular Economic pattern, and that has successfully been used. The method developed in this study can be implemented to infinite polymers, and it is of great interest for the textile industry to reduce its energy footprint.

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## ACRONYMS

CE	Circular Economy
DMC	Dimethyl carbonate
EPA	Environmental Protection Agency
FF	Feast and Famine
LA	Lactic acid
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
LOI	Limit Oxygen Index
MCL	Medium-chain-length
MMC	Mixed Microbial Culture
PA	Polyamide
PE	Polyethylene
PES	Polyester
PET	Polyethylene terephthalate
PGA	Poly(glycolide)
PHA	Polyhydroxyalkanoate
PHB	Polyhydroxybutyrate
PHHx	Poly(3-hydroxy hexanoate)
PHV	Poly(3-hydroxy valerate)
PLA	Poly(lactic acid)
PLE	Polyethylene
ROP	Ring-Opening Polymerization
SBR	Sequencing Batch Reactor

SCL	Short-chain-length
SIR	Substrate-to-inoculum ratio
VFA	Volatile Fatty Acid



# APPENDICES

## APPENDIX 1: CHEMICAL EXERGY DATA

	EXERGY (kJ/mol)	EXERGY (kcal/mol)	Reference
Cotton (C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> )	1601.895329	1079.444292	Eboh <i>et al.</i> (2016)
Water	0.75	0.505390836	Exergoecology
Acetic acid (CH <sub>3</sub> COOH)	906.46	610.8221024	Exergoecology
Propionic acid (CH <sub>3</sub> CH <sub>2</sub> COOH)	1576.57	1062.378706	Exergoecology using Gibbs
Butyric acid (C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	2251.9	1517.45283	Exergoecology using Gibbs
Valeric acid (C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> )	2890.35	1947.675202	Exergoecology using Gibbs
Others (C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> )	3544.3	2388.342318	Exergoecology using Gibbs
MMC (C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> N)	831.298113	560.1739306	Eboh <i>et al.</i> (2016)
Biomass (C <sub>1.8</sub> O <sub>0.5</sub> N <sub>0.2</sub> )	654.48	441.0242588	Song <i>et al.</i> (2011)
DMC (C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> )	1492.91	1006.004043	Exergoecology using Gibbs
Cell Membranes (C <sub>1.8</sub> O <sub>0.5</sub> N <sub>0.2</sub> )	654.48	441.0242588	Song <i>et al.</i> (2011)
PHA	2386.816307	1608.366784	Eboh <i>et al.</i> (2016)









