

## Article

# Exergy Footprint Assessment of Cotton Textile Recycling to Polyethylene

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**Abstract:** Circular economy implementations tend to decrease the human pressure on the environment, but not all produce footprint reductions. That observation brings the need for tools for the evaluation of recycling processes. Based on the Exergy Footprint concept, the presented work formulates a procedure for its application to industrial chemical recycling processes. It illustrates its application in the example of cotton waste recycling. This includes the evaluation of the entire process chain of polyethylene synthesis by recycling cotton waste. The chemical recycling stages are identified and used to construct the entire flowsheet that eliminates the cotton waste and its footprints at the expense of additional exergy input. The exergy performance of the process is evaluated. The identified exergy assets and liabilities are 138 MJ/kg ethylene and 153 MJ/kg ethylene, reducing the Exergy Footprint by 75% and the greenhouse gas footprint by 43% compared to the linear pattern of polyethylene production. The exergy requirements for producing raw cotton constitute a large fraction of the liabilities, while the polyethylene degradation provides the main asset in the reduction of the Exergy Footprint.

**Keywords:** chemical recycling; GHG emissions; Exergy Footprint; cotton textile recycling



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## 1. Introduction

Human activities require resources taken from the environment and generate waste, producing significant environmental impacts. Circular economy implementations tend to decrease that pressure on the environment, but not all cases result in footprint reduction [1]. When the recycling routes are not well designed, the pollution effects, for example, global warming, become stronger [2], and it is necessary to have means of evaluating and selecting the recycling actions in a way as to achieve footprint reduction.

Water supply and pollution become critical issues [3], causing scarcity of clean water [4], which can be partly alleviated by appropriate water management [5]. The energy aspect of water cleaning is crucial for designing efficient systems that achieve sufficient water purity and economic feasibility [6]. On the other hand, the plastics supply chains, while not suffering from a shortage of resource base yet [7], cause environmental pollution across the entire life cycle, and substitution of virgin fossil sources with waste has a significant potential for reduction of the impacts.

### 1.1. Motivation of the Current Research

Circularity implementations are necessary to alleviate the environment from the anthropogenic effects [8]. Some ideas related to circularity have been developed previously, related to reuse, remanufacturing, and recycling [9]. Circularity solutions can be significantly facilitated by using tools for environmental accounting [10]. It was found in a review from 2019 [11] that a stronger integration between circularity and sustainability indicators is necessary and that holistic innovation approaches are still scarce.

In this context, wastewater, as a problem to eliminate, can also be considered an opportunity to obtain secondary raw materials, minimising pollution.

Waste or product is not an inherent property of materials but a categorisation reflecting their economic value. A circular economy (CE) is a production-consumption pattern where waste streams become secondary raw materials [12]. The goal of the pattern is to minimise environmental impacts by extending the use of the products and materials.

There are many circularity studies concerning metals, plastics [13], wood, construction [14], energy from waste [15], as well as tools for their assessment [16]. The aim of such an analysis is to provide a global insight into a circular process and perform an evaluation to identify the environmental hotspots. Once the weak points (bottlenecks) of the cycle are identified, process modifications can be proposed to increase the overall cycle efficiency or substitute it for another process with lower impact. The main problem with implementing this type of analysis is that comparing streams is difficult due to the multitude of footprints and impacts to be evaluated alongside the stream properties. Therefore, a unifying quantification metric of the potential process improvement is necessary that would provide a clear criterion of whether certain measures constitute progress in the desired direction and enable decision making for system operation, modification, and design.

### 1.2. Circular System Performance Indicators—Environmental and Exergy Footprints

Suitable widespread indicators for measuring environmental impact are the environmental footprints. Following the guide to environmental footprints [17], a key indicator of atmospheric pollution and its effects on the climate is the GHG footprint, also referred to as “carbon footprint.” In a similar way, water footprint has been defined to quantify water depletion and pollution, motivated by clean water scarcity problems. These indicators have been useful to assess the unsustainability of the linear economy pattern of “take → make → dispose of” because human society, for a long time, has been consuming resources at a higher rate than the environment can replenish [18]. The footprint concept can be applied to any resource, e.g., energy footprint expresses the cumulative energy use of a particular product or process within a given context [19].

Obtaining a sufficiently complete picture of the considered system’s overall effect requires the quantitative evaluation of many footprints. A possible approach is to obtain a weighted combination of the selected footprint indicators, including CO<sub>2</sub> and GHG, use of fossil fuels, water, and energy consumption, etc. [20]. However, in many cases, the assignment of the weights or the scaling factors for calculating such an indicator is subjective. Instead of assigning arbitrary weights and factors, an exergy-based indicator can be used, as suggested by Varbanov et al. [21]. In that work, exergy is used as a unified criterion based on the comparable workflow assumption that the waste outputs of a process system are brought to a specified neutral state, exploiting the patterns of material flow circularity and energy cascading through terrestrial systems. The energy-based evaluation is performed using exergy for accounting for both the quantity and the required energy quality. Thermo-mechanical exergy considers the temperature and pressure of the streams, and chemical exergy takes into account the exergy extractable from a waste stream. Therefore, exergy allows summarising the mass and energy resources required and lost from a process at a planetary scale. An added benefit of using this criterion is to account for the available driving forces within a process, carried by the process streams, allowing to target the reduction of external resource use. Exergy as a criterion does not substitute other specific environmental footprints, e.g., GHG footprint [22] for global warming and water

footprint [17] for local water scarcity. Instead, it drives the process-improvement measures to reduce the impacts tracked by the environmental footprints.

Steffen et al. [23] established the planetary boundaries concept that includes nine boundaries whose transgression leads to unsafe operating space for humanity. Four of these boundaries have already been transgressed: climate change, biosphere integrity, biogeochemical flows, and land-system change. The pressure on the planet increases due to population growth, and a suitable life standard does not alleviate this situation [24]. A high level of inequality negatively affects the spread of innovations, consequently harming the environmental technologies' development [25].

A review of the life cycle assessment methodological decisions for assessing the current shift from petrochemical plastics to bioplastics shows that although all of them consider climate change, only around one quarter explores the land-system change [26]. Besides climate change, which is usually assessed by the carbon footprint, the second impact category treated in the literature is the biogeochemical flow, which is considered by around two-thirds of the studies. Before the year 2007, the use of carbon footprint assessment was almost negligible, and the environmental impact was focused on the local-scale ecological footprint [27]. Water and energy footprints followed the carbon footprint trend but at a lower awareness and use.

The Exergy Flow Diagram was used by Biondi and Sciubba [28] to visualise how and at what penalty the primary exergy inflows to an economy (with fossil fuels, renewables, ores, harvested food, and other goods) are transformed. Exergy equivalents for preventing compensating the specific pollution and toxicity impacts are used in [29] to represent the various indicators on a common basis. The Exergy Footprint was used in [30] to quantify the benefits from two alternative waste processing routes. Exergy can address several social issues—economics, ecology, sustainability, and energy policy [31].

Despite the clear usefulness of the indicator, the literature on the Exergy Footprint of circular processes is scarce. It has been applied as a sustainability indicator in the agri-food industry [32] and to ancient hominids extinction [33]. Caudill et al. [34] proposed to compare the carbon footprint and Exergy Footprint per capita of different countries. In some cases, certain direct relationships between GHG and Exergy Footprints are observed, e.g., in China, the UK, Saudi Arabia, and the USA, but not for other cases, such as, e.g., in Sweden or Japan.

The recent overhaul of the Exergy Footprint concept by Varbanov et al. [21] has provided an accounting tool to evaluate both the thermodynamic feasibility of the process systems and their approximate sustainability contribution. It can be especially useful to apply Exergy Footprint as the link between multiple footprints. Combining individual footprints produces multi-objective optimisation problems [35] where the individual objectives are difficult to weigh. Once the main environmental impacts are identified, recovery and reuse measures, such as heat integration [36], should be applied to decrease them. In this context, Exergy Footprint can be a unifying measure, allowing to achieve good initial solutions, which can be then passed to the multi-objective optimisation models.

### *1.3. Research Gaps in the Area of Textile Materials and the Potential Role of Exergy Footprint*

Circular Economy (CE) developments were analysed in [37], noting the need to understand that this is only a means of reducing the environmental impacts and that key issues still need to be measured. The majority of published works on CE do not consider an entire closed cycle where a residue becomes a raw material again. These works focus on subsets of the pattern for “reduce-reuse-recycle-replace.” That is aggravated by often low landfilling fees that discourage the investment in CE solutions, making circular solutions more expensive than landfilling [38].

For instance, the implementation of the end-of-life vehicle regulations to encourage CE has achieved a material circularity index of only 0.61 due to the relatively low landfill costs in the EU [39]. A CE implementation should not start from waste handling. Instead,

the departure point has to be the initial design of the products and their capability for reuse/remanufacturing supported by favourable policies.

A life cycle assessment (LCA) study by Jeswani et al. [40] shows that chemical recycling via pyrolysis of mixed plastic waste produces a chemical feedstock that can then be reused to manufacture virgin-quality polymers. Even when it is an emerging technology, the study results indicate that this option has about 42% lower climate change impact and life cycle energy use than the direct energy recovery from low-density polyethylene. For most other impact categories, such as acidification and eutrophication, energy recovery is reported to perform better than pyrolysis due to the higher credits received for the recovered energy. Bartie et al. [41] showed for the silicon photovoltaic circular economy that even if material loops could be closed, total circularity is impossible when exergy destruction is accounted for. There is an inevitable dissipation of energy in any process, which has to be compensated by exergy input from external sources. There are many examples of circular economy assessment in the construction and metal industry, but this study focuses on biochemical processes, especially in the textile industry.

The textile industry is of particular interest to engineers and manufacturers due to the many residues with the potential for reuse and recycling. According to Sillanpää and Ncibi [42], the textile industry is responsible for 5% of the total waste worldwide. In 2015, 16 Mt of textile waste was generated in the USA. About 15.28% was recycled and 19.03% incinerated, but most was landfilled [43]. Textile recycling is mainly performed by turning the waste into non-woven products. A life cycle analysis (LCA) of textiles in France [44] concluded that the GHG footprint had reached 442 kg CO<sub>2</sub>eq/y/capita. The possible measures to decrease this impact include avoiding unsold goods, implementing eco-design approaches, and enhancing the value of end-of-life products, including the circular economy. A blog post [45] based on a broad survey of data sources confirms the structural problems and the importance of tackling the textile industry waste, starting from over-consumption, the high consumption rate of raw materials, water pollution, and waste release, leading to the final contribution of 10% to the global GHG emissions.

The fast-fashion cycle and cheaper textile products have led to an enormous increase in post-consumer textile waste. That makes it necessary to at least partially recover some of the materials or energy contained in the waste, such as cotton and polyester (PET) waste blend valorisation to recycled PET and ethanol [46]. Biotechnology can aid a transition to a circular economy, transforming mixed waste into higher-value materials [47].

The circular economy pattern is based on four main pillars [37]: (i) Tackling the growth of material stocks; (ii) defining clear criteria for ecological cycling and eliminating unsustainable biomass production, (iii) integrating the decarbonisation of the energy system with the circular economy, and (iv) prioritising absolute reductions of non-circular flows over maximising (re)cycling rates.

Based on the performed review, several key points can be summarised:

- (a) The need for comprehensive circularity; the 10R [38] is apparent.
- (b) The global picture and circularity goals in industrial and business processes have been discussed and analysed [38].
- (c) Various footprints are available, but to apply them jointly requires subjective weighting or normalisation, as the footprints are diverse.
- (d) CE research is focused on maximising the process circularity, struggling to obtain measures for process improvement or how much circularity to apply.
- (e) Exergy profit and Exergy Footprint concepts have been formulated [21], building upon the previous Exergy Footprint ideas [33].

Several research gaps have been identified:

- Most circular economy studies do not consider entire closed cycles.
- The process and product design have to be integrated to enable using more degrees of freedom.
- It is necessary to account for the various circularity levels, such as product reuse, mechanical recycling, chemical recycling, etc.

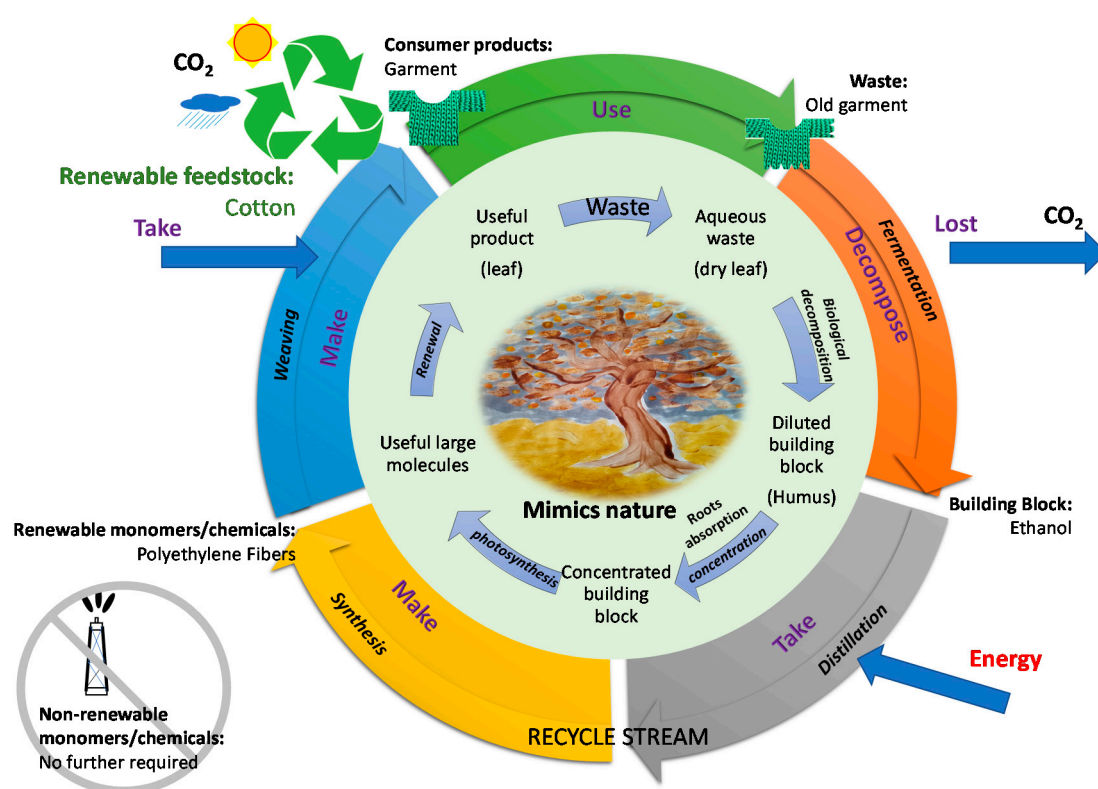
Based on the analysis, this study formulates a procedure for designing workflows that close the resource-product-waste-resource cycle. The procedure is based on the application of the Exergy Footprint concept to evaluate the potential benefit from circular processes and guide the design. The Exergy Footprint is a powerful tool to boost the circular economy, showing the advantages of the circular process schemes and determining the weak points of the cycles to be improved, based on the understanding of the fundamental trade-off between increased material flow circularity and its exergy intensity. The proposed method is illustrated using a case study of waste textile valorisation.

## 2. Method

The method presentation starts with the formulation of the main concept, scientific hypothesis, and applied procedure.

### 2.1. Modeling Concepts

The base concept used in the current method is to take as examples the natural material geo cycle [48] and other natural cycles; a thorough discussion on the antecedents of the circular economy concept can be seen in [49]. The linear economic model is unsustainable, and the intuitive solution is to use the circular economic pattern (Figure 1) for simultaneously reducing resource withdrawal and waste disposal. Some plants based on this philosophy are proposed to keep the material in circulation longer before being rejected as waste, for instance, shredding the textiles to weave them again.



**Figure 1.** Circular economy as a mimic of natural processes.

However, the quality of the reused fibres is lower than the virgin fibres, which affects the final product quality. The fibre quality is determined by the length of the molecular chains of the constituting polymers, and they degrade to some extent with each use cycle. When the waste streams are biologically and/or chemically decomposed to building block molecules that are recomposed again, virgin-quality products are produced, resulting in chemical recycling. However, the sustainability of the process depends on the sustainabil-



ity level of the biological raw material and the energy supplied. The Exergy Footprint is a straightforward metric that closely correlates with the studied system's overall resource use and footprints. This allows using it as a criterion to propose circular and more sustainable processes.

Exergy accounting is taken as the framework in the current method. The thorough reasoning for using the Exergy Footprint and exergy profit has been provided by Varbanov et al. [21]. However, it can be summarised as follows:

- Material flows and mass exchange on a global (Earth) scale are characterised by natural circularity, which leads to pollution by mixing, and misdirection of waste flows.
- Energy flows are characterised by cascading and degradation patterns. They are renewable at the planetary scale, but the renewability is limited by the harvesting area dedicated to energy capture.
- Energy is the essential input to any industry and business process system. Exergy is the relevant criterion for tracking energy spending because it accounts for the ambient conditions at which the energy flows occur.

According to Farajzadeh et al. [50], exergy analysis is an excellent measurement to quantify the material and energy. This measurement considers the conditions of the system and its surrounding environment based on the second law efficiency. There are four components in the exergy analysis: kinetic exergy, potential exergy, physical exergy, and chemical exergy. Kinetic exergy is relevant where speeds are significant, such as in turbines, while potential exergy is relevant when an electrical or hydraulic system is involved [51]. In this study, kinetic and potential exergy terms can be neglected, and only physical and chemical exergy components are assessed.

## 2.2. Description of the Procedure

A full scheme of the exergy assessment steps is shown in Figure 2. A complete production chain typically consists of various individual processes. These processes are considered building blocks that can be integrated to form a larger system. There are primary materials, intermediate products, by-products, and final products involved in these systems. Therefore, the assessment starts with developing a scientific hypothesis and modelling concept, including the identification of the materials cycle and its corresponding parts. Next, the calculation of mass and exergy balances is carried out, followed by identifying exergy assets and liabilities as part of the exergy assessment. Based on the exergy assessment, a novel idea is proposed to minimise the Exergy Footprint.

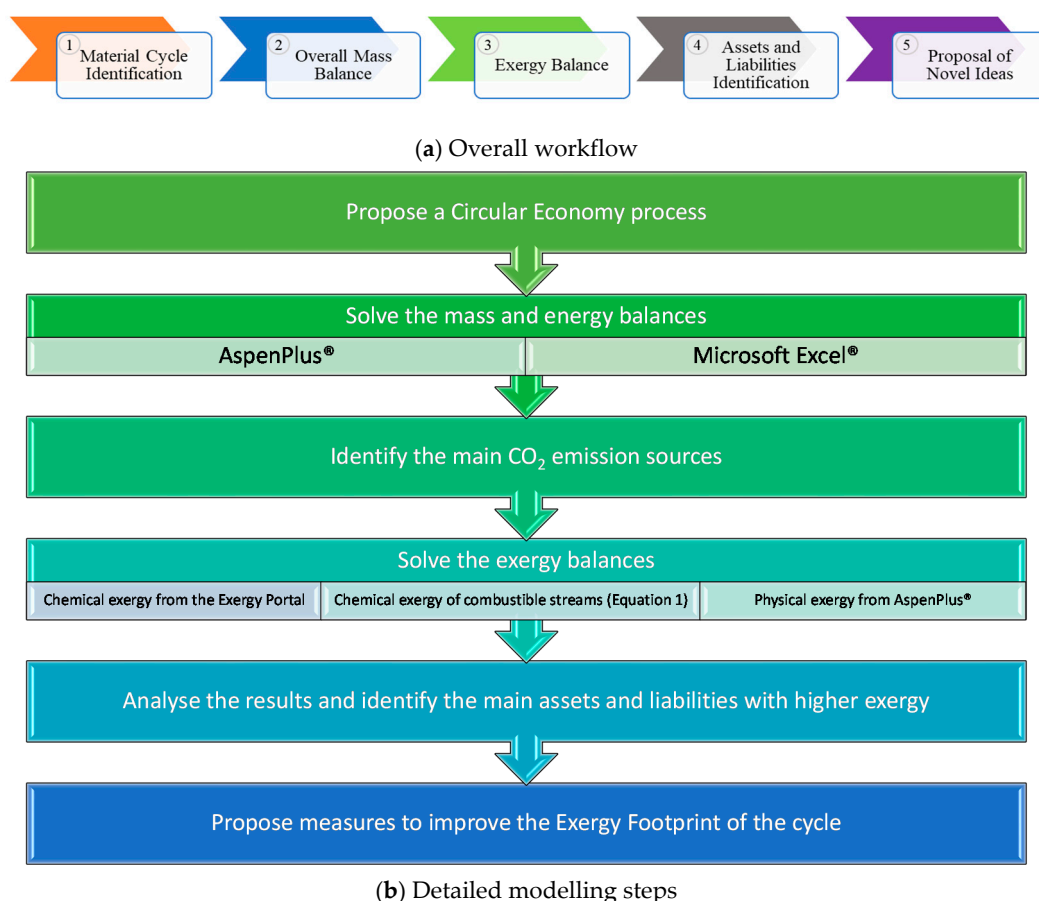
The first step is to identify the material cycle and its parts that mimic the natural cycles (Figure 1). This involves the identification of the following items:

- Service provided (e.g., tree leaf),
- The residue generated (e.g., dry tree leaf),
- Decomposition to simple building-block molecules (e.g., hummus),
- Capture and concentration of the building blocks,
- Production of complex molecules using the building block molecules.

The given items enable the identification of the cycle and possibilities of reuse and recycling in the entire cycle and waste to energy valorisation when no further possibilities of material valorisation exist. This step defines the main materials and products involved in the circular chain to obtain a basic cycle in process blocks. From here, other related materials and required driving forces (in terms of unit energy) are provided to complete the cycle. Reuse and recycling of materials and energy always play an important role. However, the recirculation limit is set due to the degradation of the material.

The second step is to solve the overall mass balances of the input and output streams of the cycle using a common calculation basis, e.g., 1 kg of product. The best available techniques and processes from the open literature are used to identify the energy requirements. As per the assumed basis of calculation, the evaluation of all streams' mass and energy balances is performed. The overall mass balances of the process steps (see Figure 3—weaving,

synthesis, water recycling) are solved in Microsoft Excel, assuming a steady state. The more complex process units, such as distillation columns and fermentation operations, are solved with Aspen Plus® [52] by setting up steady-state simulation cases. By comparing the calculations, the potential processes with a large amount of energy consumption can be determined. After that, an exergy balance of input and output streams of the entire cycle is performed, taking into account the assets and liabilities. Both physical and chemical exergy must be considered.



**Figure 2.** Steps for the exergy assessment.

The next step is to identify the assets and liabilities with a higher exergy value. Under the prevailing conditions, the liabilities must be minimised, as they correspond to consumed resources from the environment. The assets must be minimised, as they correspond to resources from society, whose available exergy should be used for the benefit of society and decreasing its impact on the environment. The last step is to propose novel ideas of minimising the calculated exergy, e.g., modifying the process, process integration, or intensification, etc. The exergy balance of the cycle indicates where the primary focus should be placed.

### 2.3. Model Description

Tightly related to the circular economy, as shown in Figure 1, a complete chemical processing diagram of polyethylene synthesis by recycling cotton waste was drawn step by step according to the modelling procedures mentioned in the previous section. The formulated concept and the procedure were applied, starting with identifying the recycling options for wastewater from cotton textile processing (Figure 3). The options were organised into several internal cycles, enacting a chemical recycling scheme. Figure 3 shows the application of the circular economy to the cotton cycle.

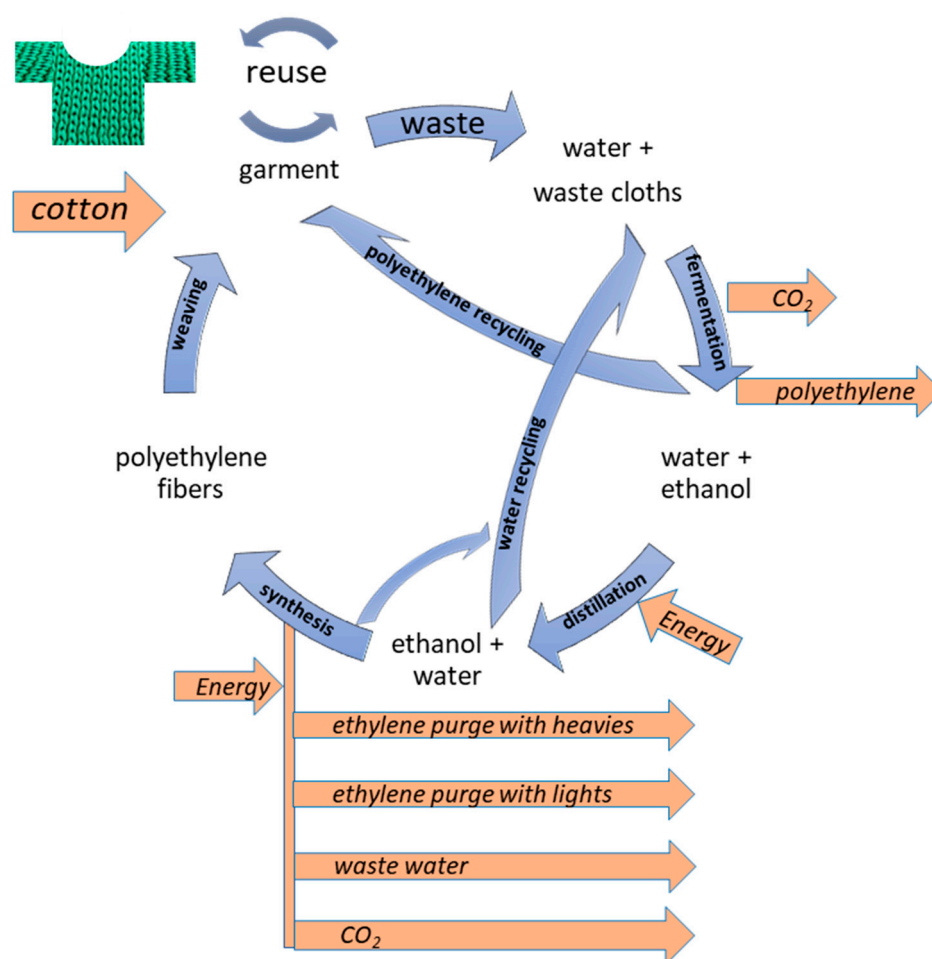


Figure 3. Model formulation.

When cotton is no longer reused via the proposed scheme, then it is discarded. Mixed waste cotton cloths with water/wastewater undergo a fermentation process in which ethanol is the main product. Unfermentable polyester fibres present in cotton are recycled, while a small portion is purged out (after ten cycles) together with the release of  $\text{CO}_2$  from the fermentation. Energy is consumed to concentrate aqueous ethanol using distillation. The separated water is mixed again with cotton waste at the beginning of the cycle. Concentrated ethanol is the secondary raw material to synthesise polyethylene fibres mixed with cotton and used in garment manufacturing.

After the complete cotton cycle proposal, mass and energy balances are required to determine the streams and unit parameters. Assuming that energy can be recovered and valorised from cotton or polyethylene waste, their exergy is calculated—see Equation (1) [53].

The fermentation step is assessed according to data of cotton conversion to ethanol, provided by Dimos et al. [54]. The ethanol concentration by distillation and the proposed alternatives to improve this step are rigorously simulated using the commercial simulator Aspen Plus® v.10 [52] with the UNIQUAC thermodynamic model and estimating the missing vapour-liquid equilibrium parameters with UNIFAC. According to the requirements of the process proposed by Tripodi et al. [55], the ethanol purity obtained is to produce ethylene from ethanol. According to Figure 3, mass flowrate is assumed constant in the cycle of ethylene to waved fibres. The produced polyethylene fibres and the recycled ones, and the input cotton provide the mass of cloths produced, which is used as the calculation basis, being the service offered to the society. The steady-state mass balances, according to the steps in Figure 3, are formulated and solved in Microsoft Excel for characterising the process. They provide the basis for calculating the exergy properties and assessing the Exergy Footprint.



Figure 2b illustrates the method followed in this study. Exergy assessment of the cycle is performed considering the physical exergy calculated following [21], and the chemical exergy is calculated using an online tool called Chemical Exergy Calculator [56]. It generates the exergy data based on the resource degradation models published in [57]. There is also a Flow Exergy Calculator available alongside the Chemical Exergy Calculator. The latter was used for most of the materials involved in this study. Since the database of the Exergy Calculator includes only reference substances, and while there was a need to calculate the exergy of some waste materials, an equation that relates natural elements and exergy was required. The Equation to calculate the specific exergy of waste polyethylene and waste cotton cloths in kJ/kg of municipal solid waste (adapted from [53]) is a function of its heating value, depending on the weight percentage of each sort of atom in the mixture (Equation (1)):

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

where  $C$ ,  $H$ ,  $O$ ,  $N$ ,  $S$ , and  $Cl$  are the number of atoms of carbon, hydrogen, oxygen, nitrogen, sulphur, and chlorine.

Aspen Plus® [52] is used as a tool for the physical exergy assessment of the interface streams—see Table 1. Based on the available thermodynamic packages available in the simulator, the exergy flow rate is available via the variable EXERGYFL for each stream. Physical exergy is  $(H - H_0) - T_{ref} \cdot (S - S_0)$ , where the reference temperature  $T_{ref}$  is in (K),  $H$  and  $S$  are enthalpy and entropy of the mixture at given conditions, and  $H_0$  and  $S_0$  are enthalpy and entropy at the reference temperature and pressure, which, by default in Aspen Plus®, are specified at 298.15 K and 1 atm. Chemical exergy is not calculated by Aspen Plus®.

**Table 1.** Exergy analysis of cycle streams for cotton fermentation and polyethylene synthesis.

Exergy to Be Added to the Process	Exergy for Ethanol Distillation (from 6% to 46% Ethanol): 35.5 (MJ/kg of Ethylene Produced) Exergy for Ethylene Synthesis: 7.1						
	Input	Output					
Mass Balances	Cotton	CO <sub>2</sub> Ferment.	CO <sub>2</sub> Vent (3OUT2) 311 *	Light Purge (5OUT3) 512 *	Heavy Purge (5OUT2) 511 *	Wastewater (1OUT2) 111–101 *	Waste Polyethylene
Pressure (bar)	1	1	1	5	5	1	1
Temperature (°C)	25	25	87.9	−71	−25	100	25
Mass flow (kg/kg of ethylene)	6	6.5	0.031	0.086	0.021	0.733	1
Enthalpy, $H$ (kJ/kg)	-	-	−6958	1383	−771	−14,340	-
Entropy, $S$ (kJ/kg/°C)	-	-	−3.45	−4.58	−4.86	−4.90	-
$H_0$ (kJ/kg)	-	-	−7725	1852	−501	−15,855	-
$S_0$ (kJ/kg/°C)	-	-	−5.81	−1.90	−3.6	−9.1	-
Mass Chemical Exergy (MJ/kg ethylene)	110.5 **	0.41	0.93	4.17	0.90	0.36	125.5 **
Total Mass Exergy (Physical + Chemical) (MJ/kg ethylene)	110.5	4.09	0.97	4.06	0.89	2.38	125.5
Mass Compositions							
Cotton	1.000	0.000	0.000	0.000	0.000	0.000	0.000
CO <sub>2</sub>	0.000	1.000	0.003	0.000	0.000	0.000	0.000
H <sub>2</sub> O	0.000	0.000	0.294	0.000	0.000	0.999	0.000
Ethanol	0.000	0.000	0.010	0.000	0.000	0.001	0.000
Ethylene	0.000	0.000	0.000	0.997	1.000	0.000	0.000
Lights (CH <sub>4</sub> )	0.000	0.000	0.703	0.003	0.000	0.000	0.000
Heavies (diethyl ether)	0.000	0.000	0.000	0.000	0.450	0.000	0.000
Polyethylene	0.000	0.000	0.000	0.000	0.000	0.000	1.000

\* From [55] by Tripodi et al.; \*\* Calculated from Equation (1).

In the linear economy model, the input cotton becomes output cotton waste, while in the proposed circular economy model, the input cotton becomes polyethylene waste (Figure 3). Both the cotton waste and polyethylene waste are combustible and can be energetically valorised.

### 3. Case Study: Exergy Footprint of Waste Cloths Fermentation to Produce Polyethylene

The case study to illustrate the methodology proposed and described in the previous chapter deals with the circular process of cotton fermentation, and polyethylene synthesis is used to demonstrate the Exergy Footprint assessment. It includes, for example, the production of the garment from crude cotton and polyethylene fibres, waste cloths fermentation, ethanol extraction, and the formation of polyethylene fibres from ethanol, etc. For the exergy calculations, the reference conditions are set to 25 °C and 1 atm. The case study description follows the implementation of the procedure in Figure 2, and the following procedure steps have the same numbering and notation.

#### 3.1. Identification of the Materials Cycle and Its Parts

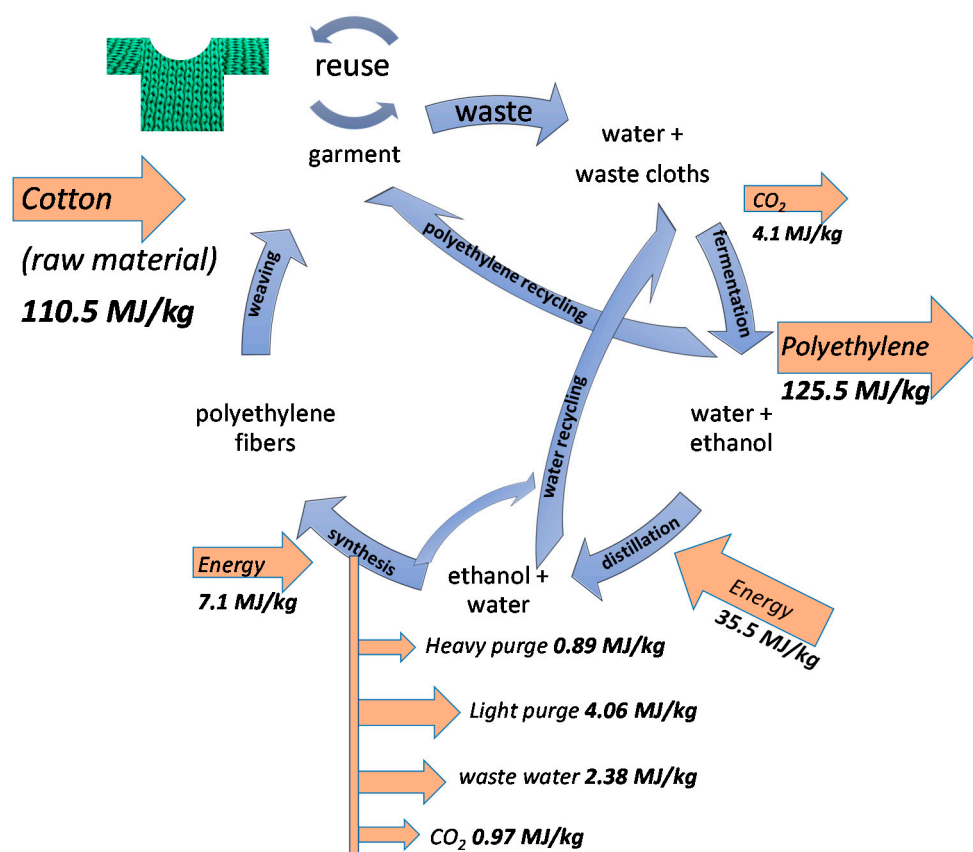
Step 1 from Figure 2a was applied. The items enumerated in Section 2.2 were identified as follows:

- (a) Service provided to the society: garment,
- (b) The residue generated considered: a mixture of cotton and synthetic fibres of polyethylene,
- (c) Building-block molecule: ethanol from cotton fibres,
- (d) Capture and concentration of the building block: distillation,
- (e) Complex molecules from building block: polyethylene,
- (f) Cycle proposal, including reuse and recycling (Figure 2),
- (g) Energy valorisation: although polyethylene can be recycled (around 10 times), finally, it becomes a residue with energy value.

Figure 4 shows the circular process scheme results. Cotton and synthetic fibres are raw materials to provide clothes to society. Waste is produced from cloths confection and after each cloth piece's end of life. This waste stream has large exergy content (a potential asset) that could be used for energy valorisation but also for mass valorisation. The fermentation of cotton can produce ethanol and release synthetic fibres that are recycled. Although polyethylene can be recycled, similar to glass or metals, after approximately ten cycles, it has to be discarded. The polyethylene residue also has high exergy content, and although at present, it is not degraded by microorganisms, it is prone to be used as raw material, e.g., plastic pyrolysis, or at least energy valorisation.

Besides thermal valorisation, polyethene waste could be used for other purposes, such as car insulation. The fermentation produces carbon dioxide and the ethanol diluted in water; the separation of the ethanol by extraction or distillation allows recycling water back to the fermentation process. Ethanol is a building block, useful to produce many other compounds, e.g., ethylene. The ethanol distillation and chemical dehydration consume energy and generate some waste output streams. The value of purge streams is low because there is a mixture of compounds, but their exergy indicates that they are useful for energy valorisation. The ethylene produced has many applications, but the polyester fibres for cloths is considered to close the cycle at the initial point.

The overview of the cycle reveals that the waste cloths are decomposed into simple ethanol molecules that, together with energy, are able to produce large functional molecules again, as already discussed in the introduction. An exergy assessment was performed to find the liabilities and assets of the overall cycle. All in all, the natural raw material, i.e., cotton, is converted to CO<sub>2</sub> and water. Energy valorisation of polyethylene residual streams would be an advisable option. The liabilities are the cotton and the energy, and the assets are the residual streams. If the energy were renewable, the overall process would be GHG neutral because the CO<sub>2</sub> emissions would be equivalent to the ones captured by cotton growing. If all the clothes were produced from natural resources, very high pressure would be produced to the environment for a large amount of land required for its production. The synthetic fibres from fossil resources alleviate the pressure on the crop field requirements, but it is not GHG neutral, and its thermal valorisation contributes to greenhouse global warming. The circular economy considers waste as raw materials minimising the environmental impact and providing alternatives to fossil resources.



**Figure 4.** The circular economy process applied to cotton waste fermentation to 1 kg of polyethylene.

### 3.2. Solve the Overall Mass Balances and Identify the GHG Emissions

Following the procedure from Figure 2 further, the balances were constructed, taking the input/output streams to/from the cycle using a common calculation basis, e.g., kg of product, and using the best available techniques or processes from open literature to identify the energy requirements.

The stoichiometric conversion of cotton to ethanol is around 54% in weight, but the yield is 52% [54]. Each 1 kg of cotton is able to produce 279 g of ethanol. Summing up the amount of CO<sub>2</sub> generated from ethanol synthesis and the amount assuming that the rest of the cotton is decomposed by microorganisms breathing, the maximum amount of CO<sub>2</sub> emissions is 1096 g. The combustion of 1 kg of cotton would produce 1630 g of CO<sub>2</sub>, and the mass valorisation does not avoid most greenhouse gas emissions. If an energy valorisation of the residual streams took place, then the CO<sub>2</sub> emissions would be the same. Consequently, the decrease in greenhouse gas emissions is not directly but indirectly connected to reducing the amount of cotton required to cover the same need. Each kg of ethanol can produce 609 g of ethylene stoichiometrically, and 170 g of ethylene is produced for each kg of cotton. If each kg of waste cotton can produce 170 g of synthetic fibres, and these polyethylene derived fibres would be recycled 10 times before disposal, then the pressure on the cotton fields to cover the same dressing requirements would be 2.9 times lower. The CO<sub>2</sub> emissions would decrease by the same amount. The process proposed by Tripodi et al. [55] to produce ethylene is considered. The main energy consumption is due to ethanol distillation and ethylene production, while the rest are negligible.

The evaluation of the GHG emissions has been performed using scenario modelling. Four alternative scenarios are compared depending on the linear process or chemical recycling pattern and the use of renewable resources or combined with fossil resources for energy generation. The common calculation basis used for all the scenarios studied is 1 kg of clothes.

The first scenario and easiest to implement is formed by the linear pattern, in which clothes are composed of 37% cotton, and the rest are synthetic fibres obtained from petrochemical sources. The energy valorisation of their waste would generate 2583 g CO<sub>2</sub>, from which 604 g CO<sub>2</sub> is assumed to be climate-neutral due to the photosynthesis during cotton growth.

The second scenario considers that the entire raw material for the clothes is only cotton. This is a renewable source, and as a first approach, it can be assumed that all the CO<sub>2</sub> emissions are neutral. The combustion of the residual cotton clothes would generate 1630 g CO<sub>2</sub>. Although the CO<sub>2</sub> emissions are reduced by 37%, neglecting the emissions from cotton agriculture, the amount of fertile land dedicated to cotton production would increase by 2.7 times, which raises issues related to deforestation. According to the US Environmental Protection Agency [58], the change of forest to crops farm produces 13.17 t/ha/y. Assuming a cotton production of 1 t/ha/y, then the CO<sub>2</sub> emissions generated by the change of land use to produce 1 kg of clothes is a very high value, i.e., 8292 g CO<sub>2</sub>.

The chemical recycling scenario presented in this study would generate the following CO<sub>2</sub> emissions for each kg of cloth produced: 406 g CO<sub>2</sub> from the fermentation process, 198 g CO<sub>2</sub> from the waste polyethylene combustion, and 25 g CO<sub>2</sub> from the polyethylene synthesis vent streams. The overall CO<sub>2</sub> emissions would be 629 g CO<sub>2</sub>. In this way, the CO<sub>2</sub> emissions are reduced by 76%, without any penalty related to land use, as the “old” cotton is substituting the fossil fuel-based fibres. However, this third scenario is considering that the energy provided for ethanol distillation and ethylene synthesis is from renewable resources without CO<sub>2</sub> emissions (83% of energy consumption is due to ethanol distillation).

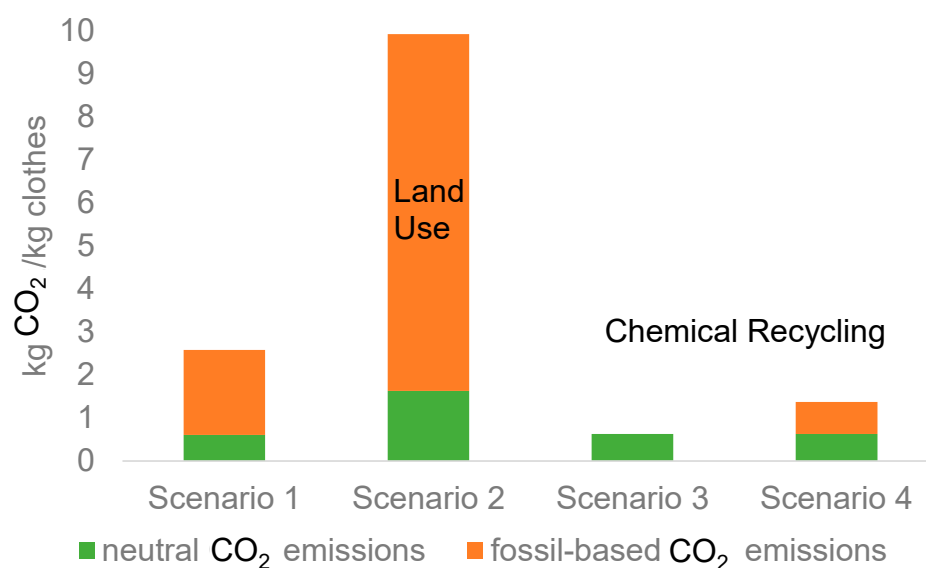
The fourth scenario is built on the basis of the third one (chemical recycling), considering that the emissions previously calculated greatly depend on the energy mix used. Assuming a value of 135 g CO<sub>2</sub>/MJ [59] due to the energy mix used, then the CO<sub>2</sub> emissions due to energy consumption are 361 g CO<sub>2</sub>. If considering only coal combustion as the sole energy source, 279 g CO<sub>2</sub>/MJ are emitted [60], corresponding to 748 g CO<sub>2</sub> due to energy generation. In this case of chemical recycling using coal combustion as an energy source, the overall emissions of CO<sub>2</sub> are 1378 g CO<sub>2</sub>, standing for a 43% CO<sub>2</sub> emissions reduction compared to the first scenario (Figure 5).

### 3.3. Exergy Balance of Input and Output Streams of the Entire Cycle

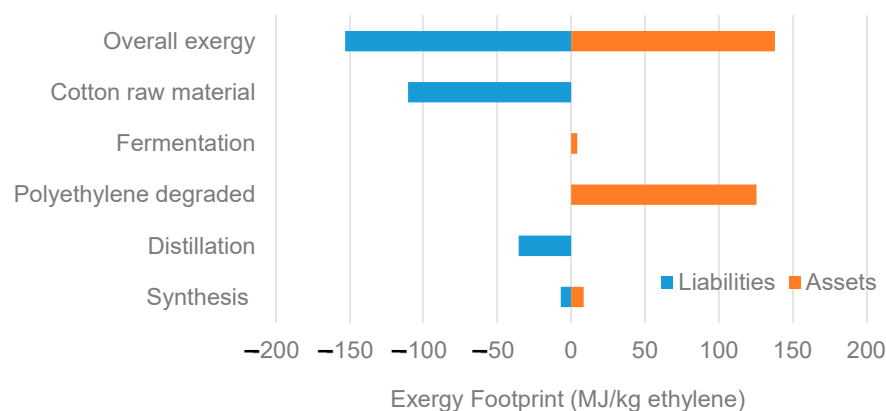
The assets and liabilities were taken into account. An exergy assessment was performed to the overall case study to determine where the leading share of resource losses impacts the environment. Only the input and output streams from the cycle were considered in the assessment, as the internal streams have no impact on the environment. The cycle streams are presented in Table 1, referring to 1 kg of ethylene produced from the waste.

### 3.4. Identification of the Assets and Liabilities with a Higher Exergy Value

The liabilities should be minimised, as they correspond to consumed resources from the environment. The assets waste has to be minimised (maximising reuse), as they correspond to resources from society, whose available exergy should be used for the benefit of the society and decreasing its impact on the environment. Both liabilities and assets are presented in Figure 6. The exergy assets are 138 MJ/kg ethylene, and the exergy liabilities are 153 MJ/kg ethylene, producing an Exergy Footprint of 15 MJ/kg ethylene [21].



**Figure 5.** GHG emissions for the linear pattern versus chemical recycling.



**Figure 6.** Exergy Footprint for the cotton fermentation cycle to polyethylene.

The exergy of the waste cotton and the residual polyethylene are similar, meaning that the residue has not lost its energy valorisation capacity. The exergy content of the other output streams is very small compared to the exergy consumption in the ethylene process and the ethanol distillation. The distillate stream contains recovered ethanol with very low purity. An increase of the distillate stream purity would decrease the energy consumption on the ethylene process and increase energy efficiency in ethanol distillation.

Therefore, the main focus to make the cycle more competitive is on increasing its energy efficiency by reducing the energy required for ethanol distillation. In practice, the clothes already have around 70% synthetic fibres mixed with natural fibres. The synthetic fibres improve the cloth properties (fewer wrinkles and longer durability) and can decrease the anthropogenic pressure on natural resources (cotton fields) if produced from textile waste. Considering that 1 kg of cotton produces 170 g of polyethylene fibres, and assuming that it can be recycled 10 times, the resulting Circular Material Use rate (CMU) is 65% [61].

### 3.5. Novel Ideas of Minimising the Exergy Footprint

A zero Exergy Footprint would be ideal for making the circular economy more realistic. As shown in Figure 6, the overall Exergy Footprint of liabilities and assets were calculated to be 153 MJ/kg ethylene and 138 MJ/kg ethylene. It is obvious that the cotton raw material contributed the largest portion of liabilities, followed by distillation and synthesis. Since the raw material is the essence of the process cycle, which was considered as having a constant Exergy Footprint unless a revolutionary raw material could be found, the focus was on



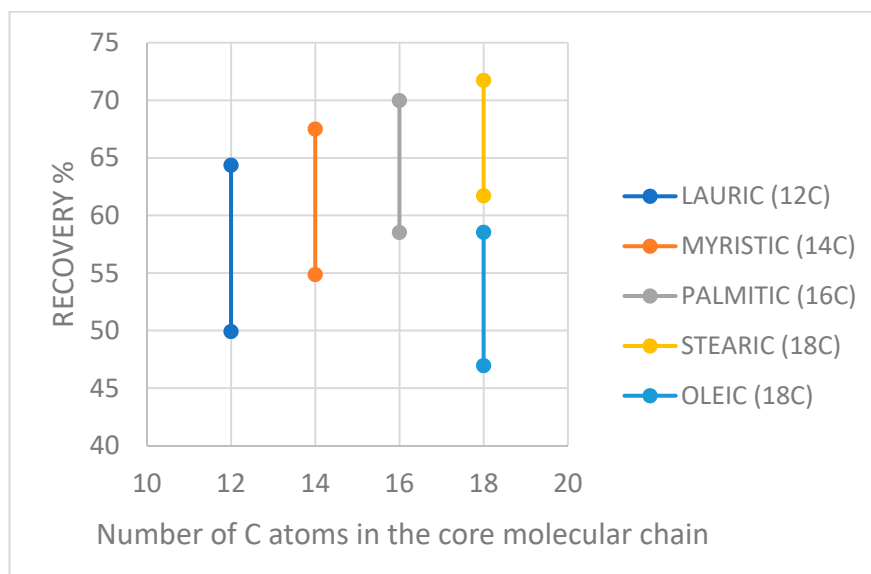
improving the chemical process and the distillation. Several novel ideas are discussed in this section to provide possible solutions to achieve the circular economy concept.

### 3.5.1. Use of Liquid-Liquid Extractive Fermentation

Liquid-liquid extractive fermentation was proposed in the 1980s for the removal of ethanol, acetone, and butanol or organic acids to avoid that inhibit the yeast [62]. Oleic acid is well recognised as a suitable solvent due to its low toxicity and favourable distribution coefficient [63]. The hydrolysis of vegetable oils produces fatty acids. Oleic acid is obtained from triolein hydrolysis, which is the main constituent of the relatively expensive olive oil. The hydrolysis of most of the oils produces mixtures of fatty acids. The suitability of liquid-liquid extractive fermentation has been proven in the literature. Still, the advantages of this approach from the energy point of view have not been assessed so far [63].

Experimental results from the literature show that oleic acid provides very good results for the extraction of fermentation products directly from the bioreactor. However, oleic acid is relatively expensive compared to using a mixture of free fatty acids produced by the hydrolysis of cheaper oils, e.g., palm oil. In addition, the possibility is considered that the oil is not totally converted.

Figure 7 shows a pair of points for each kind of free fatty acid: the lower point corresponds to pure free fatty acid, and the upper point with higher recovery corresponds to the pure oil composed of the same free fatty acids. The line between these two points corresponds to possible mixtures. It is observed that higher ethanol recoveries are attained at larger carbon chains for the fatty acid. However, the difference between them is not very large. The lauric acid (12C) is at 50% recovery, and the stearic acid (18C) is at 61% recovery. Although oleic acid has a long carbon chain, the presence of saturation decreases its effectivity. Therefore, it can be concluded that free fatty acid mixtures from other oils than the oleic acid from olive oil are recommended. According to the simulation results, non-hydrolysed oil in the solvent is also an option to be experimentally explored. The lower solubility of water in oil allows reaching higher recoveries of ethanol for a fixed ethanol/water ratio in the extract (in this case, at 1.6/1).

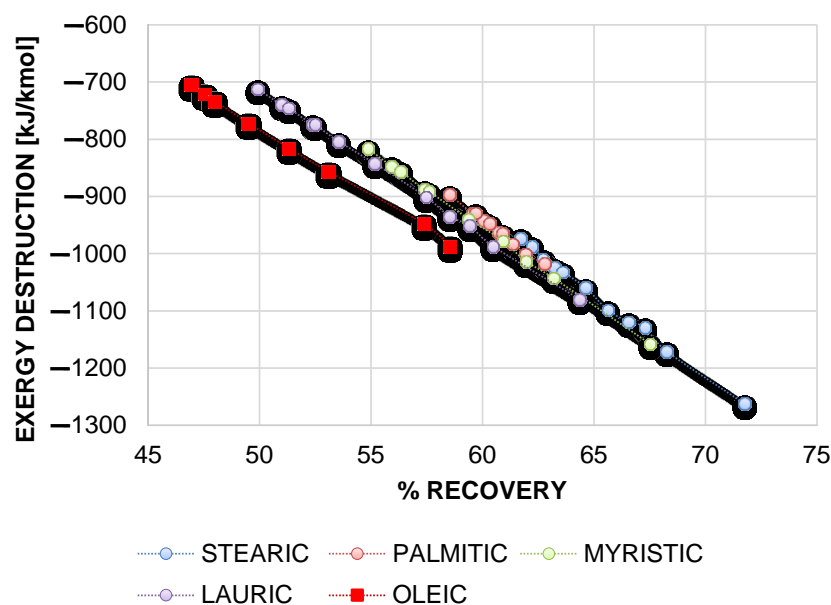


**Figure 7.** Influence of the free fatty acid chain length on ethanol recovery.

The extraction is a spontaneous process that does not consume energy but produces an exergy degradation corresponding to mixing energy. This amount of exergy becomes related to the energy that would be required to recover the solvent from recycling it to the extraction unit, and it is preferable that it be close to zero. Figure 8 shows that the use of oleic acid/triolein is a little less favourable than the saturated free fatty acids and their

corresponding oils. The different saturated fatty acids behave very similarly (Figure 8), showing a linear correlation between the exergy and the recovery (Equation (2)).

$$\text{Exergy [kJ/kmol]} = -25 \times \% \text{Recovery} + 547; R^2 = 0.9911 \quad (2)$$



**Figure 8.** Influence of the recovery on the exergy degraded by the extraction.

As it is expected, a higher recovery than a higher exergy degradation is calculated. According to exergy results, no significant differences are obtained from different free fatty acids and oil mixtures, and the use of mixtures can be more advantageous since the purification would be avoided. Mixtures of many free fatty acids are able to provide an extraction as pure oleic acid or even better.

The energy consumption of a process using a single distillation column (Figure 9a) was compared with the energy consumption of the extraction with oleic acid (Figure 9b). Both ethanol dehydration processes are rigorously simulated. The ethanol at its azeotropic composition with water is collected as the distillate at the distillation columns of both processes with 75% purity. A large number of stages, i.e., 80 and feed to 60, are used to require a value close to the minimum reflux and obtain an energy consumption compared to its minimum value. Although it is not optimal, it is enough to quantify the energy consumption of each column: the optimum reflux is around 30% higher than the minimum. For a single distillation column and a mass reflux ratio of 0.445, the reboiler energy consumption is 9412 kJ/kg of ethanol collected at the distillate. The 6% ethanol in water is fed to a decanter with the solvent oleic acid at a mass ratio of 4.36 kg recycled solvent/kg crude feed for the extraction process. About 43.4% of the feed ethanol is recovered at the extraction. In the extract, the water/ethanol mass ratio is 1.6/1.

The stream from the decanter to the distillation column has a significantly higher flow rate than a single column. Still, a large amount of water is avoided, and the free fatty acid has a higher boiling point as well. The distillation column of the extract flow from the decanter has a mass reflux ratio of 16.74 and a reboiler heating rate of 63,982 kJ/kg of ethanol collected at the distillate. This means that the extraction process consumes almost seven times more energy than a single column. With such a large difference, process optimisation is not necessary to discard the extractive process.

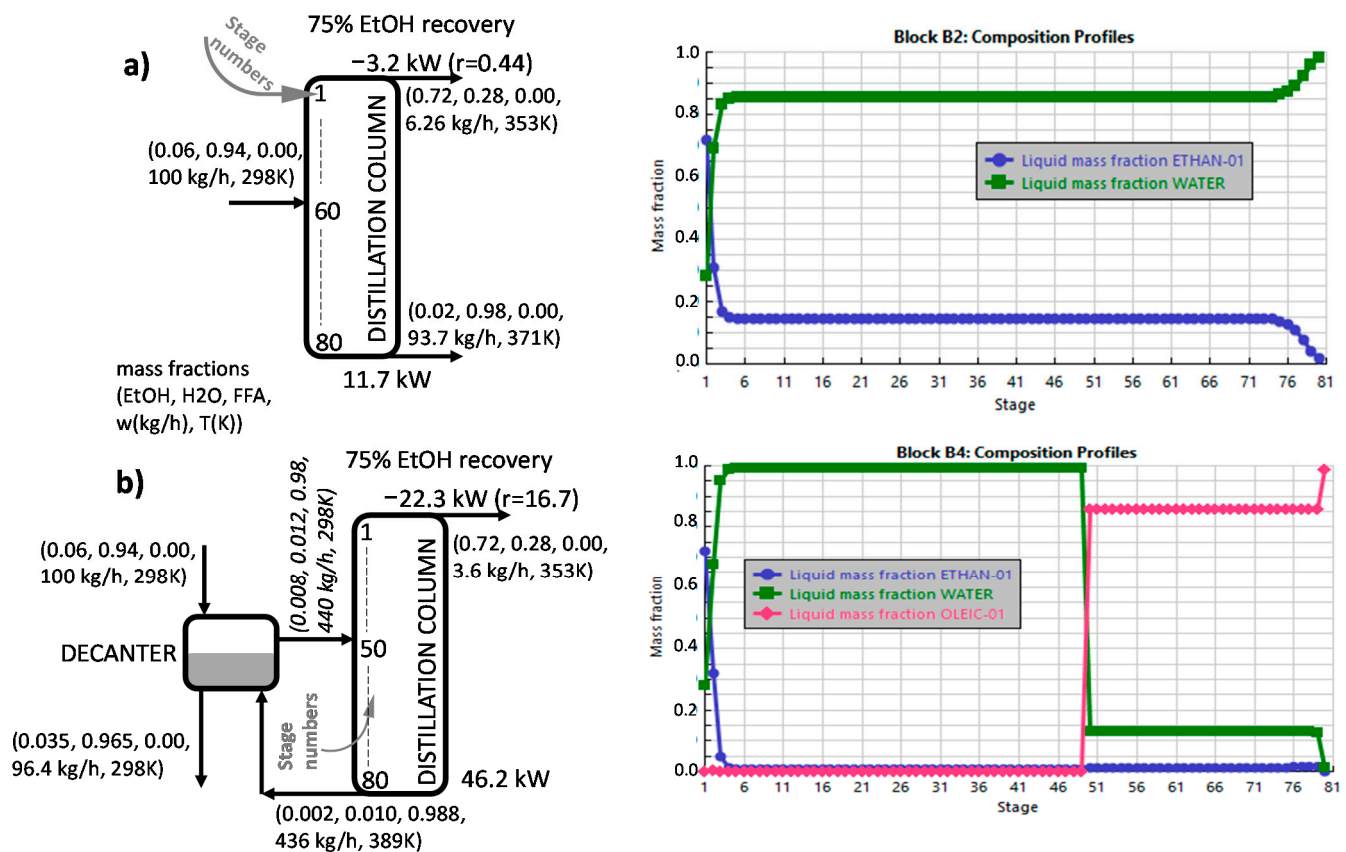


Figure 9. Process schemes for (a) a single column and (b) with extraction with free fatty acids.

This result is obtained with the implemented parameters in Aspen Plus® [52] using the APV100 database for this mixture, and UNIFAC was used for the estimation of the solubility between water and oleic acid. It is well known that oleic acid has negligible solubility in water [63]. Still, according to the UNIFAC estimation, there is some non-negligible solubility of water in the oleic acid phase (Figure 10).

Instead of considering only the oleic acid solubility in water (Figure 10 left), which is negligible, it is also important to account for the water solubility in oleic acid. The latter is small but not negligible (Figure 10 right). There are two alternative cases to analyse: (a) assuming no solubility of water in oleic acid and (b) assuming a non-negligible solubility of water in oleic acid (following the UNIFAC results).

Analysing case (a) is a quite favourable liquid-liquid equilibrium where the organic phase has a mass fraction of ethanol five times higher than the aqueous phase. In this case, the significant difference of volatilities between the oleic acid and the ethanol recommends using a flash unit instead of a distillation column. The process scheme for this case study is presented in Figure 11. The same recovery rates are used in the decanter and the flash, as for the previous calculated case. In this case, the energy consumption would be only 30% of the single distillation column, and ethanol would be recovered practically pure instead of its azeotropic mixture with water.

In case (b), based on the UNIFAC prediction that water has some solubility in oleic acid, the results are not more favourable. Using the same calculation basis as in the exergy assessment of the chemical recycling process in Figures 4 and 5 (per 1 kg of clothes), a diluted ethanol feed of 303 kg/h is used. In this case, a single distillation column has exergy of 35.5 kW with a thermodynamic efficiency of 60% [64]. However, assuming the water solubility in the extractor, then the use of the decanter produces an exergy increase to 140 kW with an efficiency of only 43%. This result is completely different than in case (a), where water solubility is negligible and where exergy decreases dramatically to only

1.5 kW, requiring a simple flash for the solvent recovery. The water solubility in free fatty acids is an important parameter that defines the suitability to use the extraction process for ethanol dehydration with free fatty acids. Following the analyses of the above cases, a further experimental investigation is required to determine the mutual solubilities of the components into the aqueous and organic phases. This has to quantify the solubility values and assess the implications for the phase equilibria and the mass flows, determining the exergy assets, liabilities, and footprint.

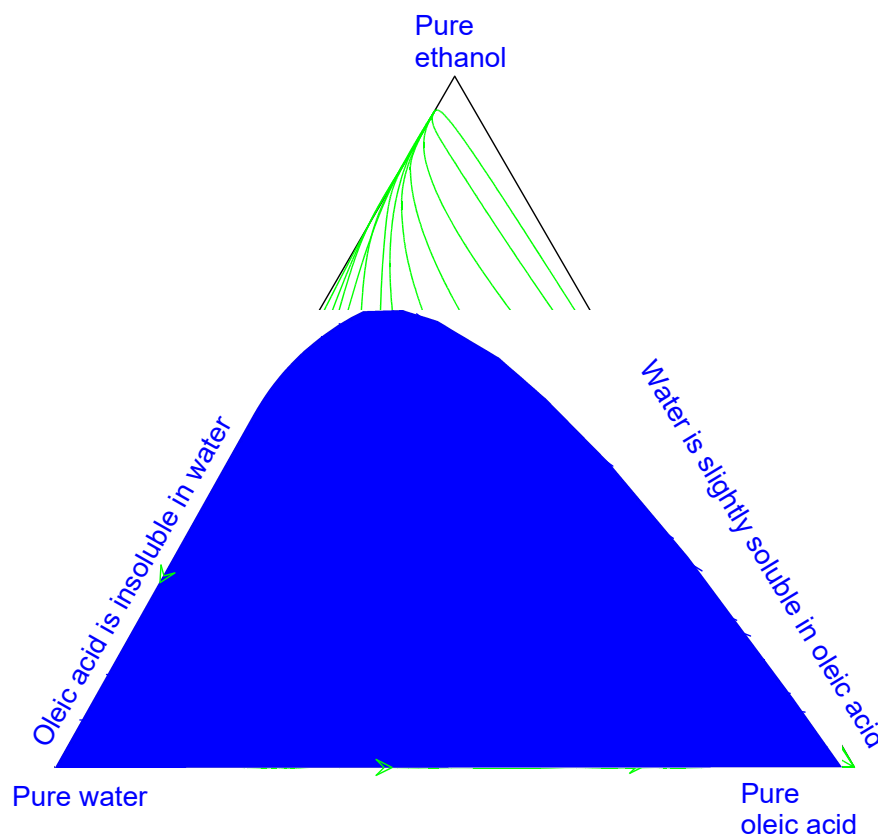


Figure 10. Residue curve map for the mixture oleic acid-water-ethanol.

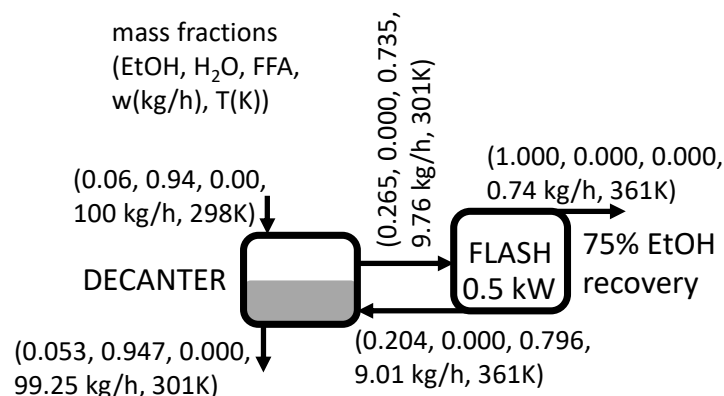


Figure 11. Process scheme when water is not present in the extract.

### 3.5.2. Separation of ABE Fermentation Products in a Single Column

The last section has proven that fatty acid extraction of fermentation products could be a very promising process depending on the amount of water solubilised in the free fatty acids. In case that some water is solubilised, then direct distillation could be more advantageous. This section proposes a novel process intensification performing the separation of

all the compounds of the ABE mixture (acetone, butanol, and ethanol in aqueous media) in a single column. It is well known that process intensification allows saving capital costs and energy. Figure 12 provides the residue curve map showing that there is a residue curve following a path from acetone: distillate stream 1—ethanol/water azeotrope; upper side stream 2—butanol/water heterogeneous azeotrope; lower side stream 3—butanol; bottoms stream 5. A side decanter can take advantage of the phase split for the butanol/water azeotrope to collect pure water as a side stream (4w in Figure 12). The residue curve maps represent the bundle of column profiles for packed distillation columns operated at an infinite reflux flow rate. Therefore, the residue curve's existence assures that this process scheme is feasible with a sufficiently high number of stages and reflux. Figure 13 shows rigorous simulation results confirming that the separation of the ABE mixture in a single column is feasible. The distillation column optimisation will be performed as future work.

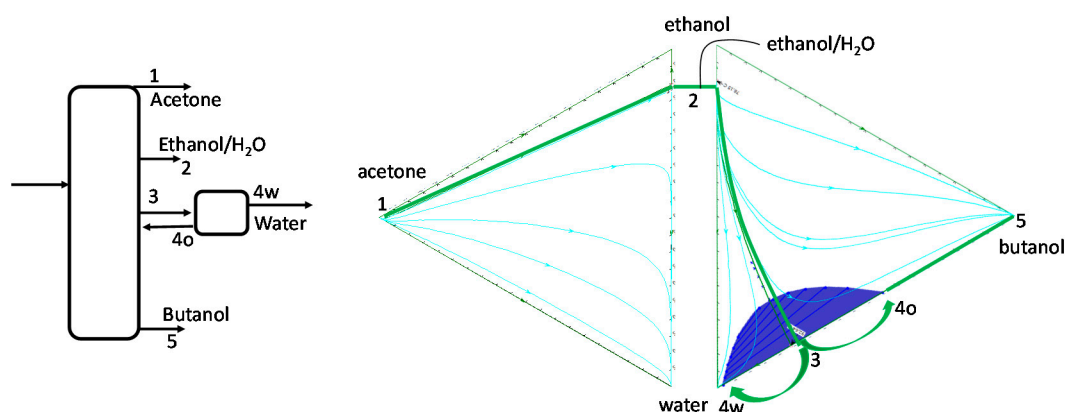


Figure 12. Feasibility of the separation of ABE mixture in a single distillation column.

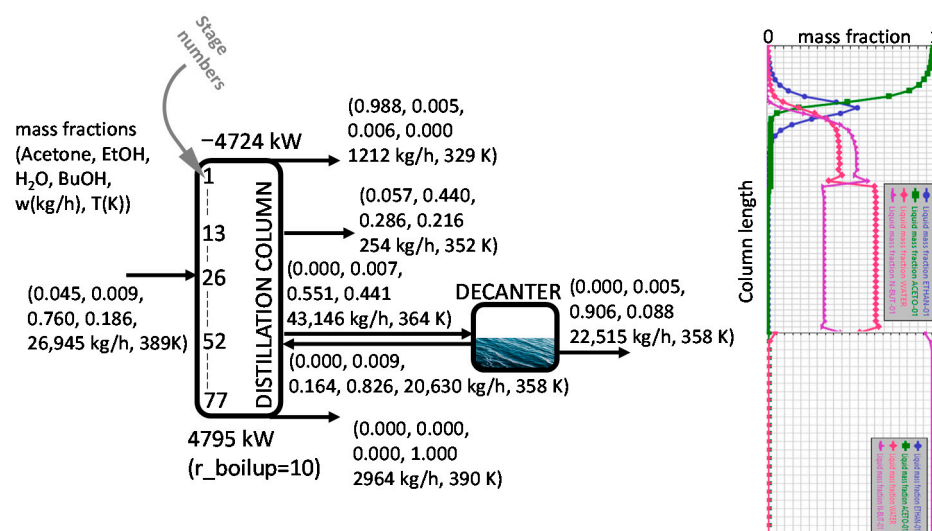


Figure 13. Rigorous simulation results prove the feasibility of a single column separation.

#### 4. Conclusions

The presented work has developed an assessment method for the application of the Exergy Footprint concept to cotton textile recycling. Exergy Footprint has been used as the fundamental concept to guide the procedure for designing chemical recycling processes. A procedure for implementing the circular economy pattern has been formulated by constructing a chemical recycling scheme from a set of available reactions and processes as unit operations. The scheme links together the unit operations into a closed system, taking feed waste cotton fibres and converting them into useful products. Exergy Footprint is



calculated based on the balance of exergy assets and liabilities of the considered process and used for the process improvement by minimising the exergy liabilities of the unit operations with a negative balance and maximising the utilisation of the exergy assets.

The results show that the Exergy Footprint family of concepts allows designing a process where clothes can be produced from sustainable materials reducing the Exergy Footprint to a quarter (25%) compared with the linear processing pattern (i.e., without the chemical recycling scheme). The resulting GHG emission reduction reached 43%.

Based on the developed novel ideas, the presented circular process can be further improved to become more competitive and with a lower Exergy Footprint. Fermentation allows the transformation of the organic waste into building blocks useful as secondary raw materials but diluted in water. The assessment shows that the separation of the fermented secondary raw materials from the aqueous media is the main step to be improved in circular processes. Some process improvements for this separation step are proposed in the current work. On the one hand, the results prove that mixtures of free fatty acids are as good as using oleic acid for in-situ extraction of fermentation products. On the other hand, a process intensification for ABE mixtures separation in a single distillation column is proposed. Experimental water solubility on free fatty acids must be determined in future work, as this variable greatly affects the process performance. After minimising the inherent energy demands of the process, further reduction of the GHG footprint should be sought in supplying waste heat and renewable energy to power the designed separation processes.

An important direction for future work is to develop a procedure for evaluation of the properties of the suggested secondary polyethylene and how well it fits the potential applications in terms of material strength, suitability for use in terms of hygiene, as well as the process feasibility and issues at scale-up.

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## Nomenclature

ABE	An aqueous mixture of acetone, butanol, and ethanol from fermentation
CE	Circular economy
CMU	Circular material use rate
EU	European Union
EX <sub>MSW</sub>	Chemical exergy of solid waste
ExFP	Exergy Footprint
GHG	Greenhouse gases
LCA	Life cycle analysis
PET	Polyethylene terephthalate
UNIQUAC	UNIversal QUAsi-Chemical thermodynamic regression model
UNIFAC	Universal quasi-chemical Functional group Activity Coefficients
USA	United States of America

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