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Evaluation of Biogas Production from Anaerobic Digestion of Biopolymeric Films and Potential Environmental Implications

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Abstract: The increasing environmental pollution resulting from plastic waste and the need to reuse agro-industrial wastes as a source of discarding has led to the development of innovative biobased products. In the frame of this context, the use of neat polylactic acid (PLA) and its blend with polybutylene succinate (PBS) with or without cellulose nanocrystals (CNCs) extracted from hemp fibers is explored here. This study aimed to assess the biogas production of different biopolymeric films. In parallel, life cycle assessment (LCA) analysis was performed on the same films, focusing on their production phase and potential end-of-life scenarios, regardless of film durability (i.e., single-use packaging) and barrier performance, to counteract possible soil health threats. Specifically, this study considered three specific systems: PLA, PLA_PBS (PLA/PBS blend 80:20 *w*/*w*), and PLA_PBS_3CNC (PLA/PBS blend + 3% CNCs) films. The assessment involved a batch anaerobic digestion (AD) process at 52 °C, using digestate obtained from the anaerobic treatment of municipal waste as the inoculum and cellulose as a reference material. The AD process was monitored over about 30 days, revealing that reactors containing cellulose showed inherent biodegradability and enhanced biogas production. On the other hand, biopolymeric films based on PLA and its blends with PBS and CNCs exhibited an inhibitory effect, likely due to their recalcitrant nature, which can limit or delay microbial activity toward biomass degradation and methanogenesis. LCA analysis was performed taking into consideration the complex environmental implications of both including biopolymers in the production of renewable energy and the use of post-composting digestate as an organic fertilizer. Remarkably, the PLA_PBS_3CNC formulation revealed slightly superior performance in terms of biodegradability and biogas production, mainly correlated to the presence of CNCs in the blend. The observed enhanced biodegradability and biogas yield, coupled with the reduced environmental impact, confirm the key role of optimized biopolymeric formulations in mitigating inhibitory effects on AD processes while maximizing, at the same time, the utilization of naturally derived energy sources.

Keywords: biopolymers; polylactic acid; polybutylene succinate; cellulose nanocrystals; anaerobic digestion; biogas; biomethane; environmental impact; life cycle assessment

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1. Introduction

Food packaging contributes approximately 5.4% to global greenhouse gases (GHGs) emissions, with sector-specific impacts varying widely: up to 40% for alcoholic beverages; 10–20% for fresh produce; 10–12% for dairy, fruits, vegetables, and nuts; and around 2% for meat, fish, and eggs [1]. The growth in the global population (about 10.3–10.5 billion by 2050 and about 12.0–12.6 billion by 2075 [2]) together with the increasing need for food

has increased the production of single-use plastic packaging systems (23 million tons just in Europe; projections estimate 92 million tons by the year 2050 [3]), whose life cycle is noticeably short, as they quickly become waste to be disposed of. This scenario has increased the production of plastic waste and the food packaging presence in waste streams [2,4]. To address this issue, the European Commission introduced Directive 2008/98/EC (Waste Framework Directive) [5], requiring European Union member states to follow a waste management hierarchy based on five levels:

1. Prevention;
2. Reuse;
3. Recycling;
4. Other recovery;
5. Disposal.

In the last years, biodegradable polymers have been considered as a reliable alternative to non-degradable ones, also due to the need to solve the problems generated by plastic waste at their end of life [6]. Polylactic acid (PLA) is one of the most important biobased polymers obtained from renewable resources [7] and used in food packaging [8]. It is derived from renewable resources, such as corn starch or sugarcane [9], and exhibits excellent mechanical properties, thermal stability, and biodegradability, making it a suitable alternative to conventional petroleum-based plastics. However, its inherent brittleness and low thermal resistance limit its applications [10]. To overcome these limitations, PLA is often blended with other biopolymers, such as polybutylene succinate (PBS), which is also derived from renewable resources [11] and possesses good mechanical properties and thermal stability, which make the blend more suitable for food packaging applications [12,13]. PBS is an aliphatic polyester that is attracting attention due to the possibility of biobased production, its intrinsic biodegradability, as well as its good processability [14].

In comparison to equivalent traditional polymers used in food applications, many biopolymers show some limitations, such as poor oxygen barrier characteristics and relatively poor thermal and mechanical properties [15,16]. In this context, the development of nanocomposites represents a valid method to increase the physical properties of biodegradable polymers. Recent studies highlighted how using nanocomposites has been an efficient strategy to upgrade the structural and functional properties of biodegradable polymers. The incorporation of organic and inorganic nanofillers, such as nanocellulose, nanolignin, nanohydroxyapatite, metallic nanoparticles, or carbon nanostructures, into biodegradable polymers like PLA or poly(ε-caprolactone) (PCL) has been tested to produce nanocomposites with enhanced mechanical, thermal, and electrical properties [17–19]. Cellulose nanocrystals (CNCs), among the nanoparticles employed as reinforcements for biobased polymers, are gaining increasing interest. In this regard, CNCs can be obtained as monocrystalline domain-based stiff rods, with diameters ranging from 1 to 100 nm and from 10 to 100 nm in length. These nanocrystals can be produced through the acid hydrolysis of plant fibers, where sulfuric acid is employed to remove the amorphous plant components, with the formation of highly crystalline cellulose [20].

Moreover, the problem related to food packaging waste recycling (also packaging based on biopolymers) is that this type of packaging is often highly contaminated with food residues, oils, and other impurities, which can significantly complicate the recycling process, although mechanical recycling is technically feasible [21]. In any case, biodegradable polymers represent a valid resource from a sustainable perspective due to the possibility of helping divert food waste from landfills thanks to their composting features. Bioplastics offer indeed significant advantages, helping to mitigate the environmental impact associated with conventional petrochemical-based plastics. PLA and other biodegradable polymers are derived from renewable resources like corn starch and sugarcane, and they can be composted industrially, thus reducing persistent plastic waste accumulation in the environment [6,22]. Additionally, bioplastics can enhance the sustainability of food packaging without compromising essential properties such as mechanical strength and barrier functions against oxygen and moisture [23]. Furthermore, the incorporation of

nanomaterials, such as CNCs, can improve these properties, making bioplastics competitive with conventional polymers [24,25].

Bioplastics' biodegradability makes them suitable for the collection in the organic fraction of municipal solid waste (OFMSW) [26]. Specifically, their biodegradability in anaerobic environments allows for biogas to be produced, contributing to renewable energy production and sustainable waste management [27,28]. Anaerobic digestion (AD) can have the double advantage of both producing biogas used in the electricity industry and biomethane, which can be recovered by suitable purification procedures and fed into the natural gas network or utilized for the transportation sector [29,30]. The use of bioplastics in food packaging not only reduces environmental impact but also supports a more sustainable circular economy, aligning with global efforts to reduce plastic pollution and promote the use of renewable resources [31,32].

In this regard, life cycle assessment (LCA) analysis is widely recognized as one of the tools to assess environmentally critical issues of processes and products and suggest solutions aimed at improving the related environmental performance [33,34]. It can be considered as the leading tool to assess bio- and non-biopolymer-based packaging environmental performance. An LCA approach applied to a specific industrial system is aimed at focusing on the related hotspots and at proposing improvements of the environmental efficiency by means of a rationalization of natural and human resources [35]. Moreover, the study also allows for comparing the environmental performance of different industrial systems, products or, within the same industrial system, technologies. This can be achieved through the development of specific models of the analyzed system by considering the boundaries of the system, the involved processes and sub-processes, and input and output flows crossing the process. The assessment begins with raw material extraction and considers all aspects of production, use (or service life), and end of life. The study must be based on the LCA methods described in ISO 14040 and 14044 [36,37], and it has to be divided into four steps: (1) definition of the goal and scope of the study, (2) establishment of a life cycle inventory (LCI), (3) life cycle impact assessment (LCIA), and finally, (4) interpretation of environmental burden associated with the product. The environmental aspects generally include energy expense, resource exploitation, and emissions (in air, water, etc.), while environmental impact categories generally include climate change, particulate matter formation, eutrophication, land use, as well as human carcinogenic and non-carcinogenic toxicity.

In this regard, this paper aimed to investigate the possibility of producing renewable energy (biogas) through the thermophilic AD of biodegradable polymer-based films inoculated with digestate derived from the anaerobic treatment of the OFMSW, as well as the related environmental sustainability. The AD of food waste and waste bioplastics is indeed a field of growing interest thanks to the fact that the digestion of bioplastics can generate CH_4, which is considered a promising source of renewable energy [35], thereby presenting an opportunity to utilize bioplastics as potential contributors to sustainable energy production. Three different biopolymeric films were tested for about one month in batch anaerobic reactors, i.e., a film based on only PLA, a blend made of PLA and PBS 80:20 (*w/w*) (PLA_PBS), and the same blend added with 3% of CNCs (PLA_PBS_3CNC). A proportion of 20% of PBS was chosen according to a previous study that highlighted it as a valid compromise to maintain good thermal and mechanical properties of the PLA films, while 3% of CNCs was selected to enhance the biofilm disintegration behavior tested under composting conditions according to ISO 20200:2015 [13,38]. At the same time, attention was paid to the biodegradability assessment during the process. Meanwhile, LCA analysis was performed in order to evaluate the impacts and feasibility of the process in order to assess the potential and limitations of using the aforementioned biofilms in the food packaging industry. It is worthwhile pointing out that no economic or social impacts were considered and an attributional LCA was performed both in the case of the production stages of the bioplastic-based films and on the related end of life.

2. Materials and Methods

2.1. Cellulose Nanocrystal (CNC) Production

Cellulose nanocrystals (CNCs) were extracted from *Phormium tenax* technical fibers [20]. The latter were pre-treated with 0.5% (*w*/*v*) NaOH solution, washed with distilled water several times, and dried in an oven at 80 °C for 24 h. After this stage, they were chopped to an approximate length of 5–10 mm and de-waxed, boiling the fibers in a mixture of toluene/ethanol (2:1 *v*/*v*) for 6 h. The obtained fibers were filtered, washed with ethanol for 30 min, and dried. Regarding cellulose extraction, natural fibers were treated with 0.7% (*w*/*v*) of sodium chlorite and the fibers (liquor ratio 1:50 *w*/*v*) were boiled for 2 h. The solution pH was lowered to about 4 by means of acetic acid. System treatment with sodium bisulfate solution at 5% (*w*/*v*) was carried out and, at the end of this preliminary process, holocellulose (α-cellulose + hemicellulose) was obtained, as a result of lignin removal. The holocellulose was processed with 17.5% (*w*/*v*) NaOH solution, filtered, and washed with deionized water. The obtained material was dried at 60 °C in a vacuum oven until constant weight was measured.

CNC suspension was then obtained from pre-treated *Phormium tenax* leaves by sulfuric acid hydrolysis. The lab-scale process was carried out with 64% (*w*/*w*) sulfuric acid at 45 °C for 30 min with high rate stirring. After the acid removal, dialysis, and ultrasound treatment, an ion exchange resin (Dowex Marathon MR-3) was added for 48 h and then removed by filtration.

CNC suspensions were neutralized by the addition of 1.0% (*v*/*v*) of 0.25 mol L^{-1} NaOH. The final CNC production yield was about 10% with respect to the dry initial source.

2.2. Biopolymeric Film Preparation

PLA, PLA_PBS, and PLA_PBS_3CNC films were prepared by using a co-rotating twin screw micro extruder (DSM Explorer 5&15 CC Micro Compounder, Xplore Instruments BV, Sittard, The Netherlands). The used apparatus is equipped with a film casting system, suitable to produce 70 mm wide film strips. The film thickness was around 150 µm. PLA pellets were previously dried in a vacuum oven at 98 °C for 3 h, while PBS ones were dried at 80 °C for 12 h. Moreover, CNCs were dried at 40 °C overnight.

For the production of PLA film, a screw speed of 150 rpm and mixing time of 1 min were implemented, while a temperature profile from 180 °C to a maximum mixing temperature of 210 °C was chosen. The same process was applied to produce the neat PLA/PBS blend (weight ratio 80:20 *w*/*w*). The only difference regards the mixing rate, which in this case amounts to 6 min. This time was reduced to 4 min in the case of the PLA_PBS_3CNC film (PLA/PBS blend 80:20 *w*/*w* as a matrix, filled with the 3% wt. of CNCs) to prevent CNC degradation.

Figure 1 summarizes a schematic representation of the film extrusion process. After the drying phase, each component of the investigated systems is fed into the micro-extruder, where both the polymer blends and the nano-reinforced compounds are recirculated through a specific channel whenever the extrusion die is hindered by the activation of the lock. At the end of the mixing time, the lock is removed, and the polymer melt can go through the extrusion thin die. At the exit of the die, the (molten) polymer sheet is cooled down by an air knife and subsequently captured by the first roll and driven through a second roll, where it is wound and collected. The roll system, through the speed and the torque regulation, is responsible for the film stretching in the winding direction (no cross-sectional stretching).

It has to be pointed out that the film stretching mainly occurs between the extrusion die and the first roll.

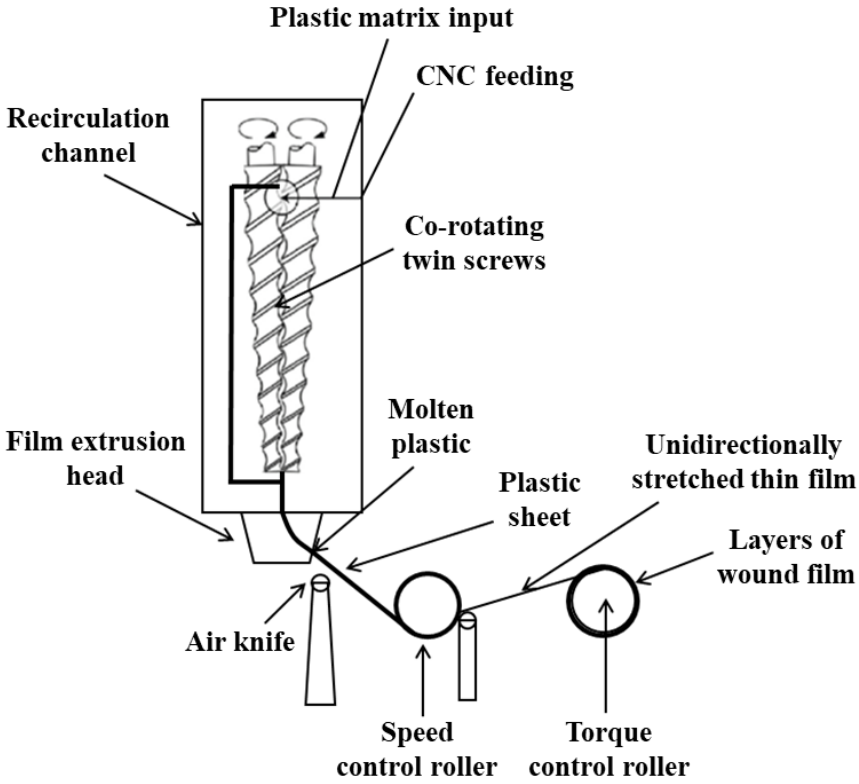

Figure 1. Schematic representation of the film production through extrusion and casting.

2.3. Batch Anaerobic Digestion (AD) Test

A batch AD test was conducted at a temperature of 52 ± 2 °C using digestate obtained from OFMSW treatment as the inoculum. A reference material (cellulose films) and three treated samples were set up in the batch AD reactors as follows: sample with cellulose as reference material consisting of inoculum added with cellulose films; PLA sample consisting of inoculum and PLA films; PLA_PBS sample consisting of inoculum and blended films made of 80% PLA and 20% PBS; and sample PLA_PBS_3CNC consisting of inoculum and blended films made of 80% PLA and 20% PBS added with 3% CNCs. A control sample was represented by the mere inoculum. The bioplastic films and the reference material were shredded into fragments of 1.5 × 1.5 cm to provide 1 g of total solids (TS), equivalent to the dry weight (DW) of the material, which was then added to 67 g of wet inoculum according to ISO 15985:2014 [39]. The production of biogas was evaluated daily through the volumetric method over a period of about 30 days and biodegradation was subsequently estimated. As far as the percentages of bio-CH_4 in the biogas produced from different samples are concerned, they were obtained from data in the literature [40,41]. The test was conducted in a tank equipped with a thermostatic unit to maintain the temperature. Inside the tank containers with a capacity of 300 mL were placed. Each container, once filled with the respective material (inoculum, inoculum + cellulose, inoculum + bioplastic), was connected to a hydraulic gasometer represented by a second container filled with water through a capillary tube that was in turn connected to a third container (graduated cylinder). The pressure increase due to biogas production caused the water to move from the second container to the graduated cylinder, allowing for quantification of the biogas volume produced (Figure 2) [29,42,43].

The daily volume of water displaced corresponded to the biogas production, expressed in Nm^3/t of dry matter. Each sample was analyzed in triplicate. The main chemical characteristics of the digestate used as inoculum are reported in Table 1.

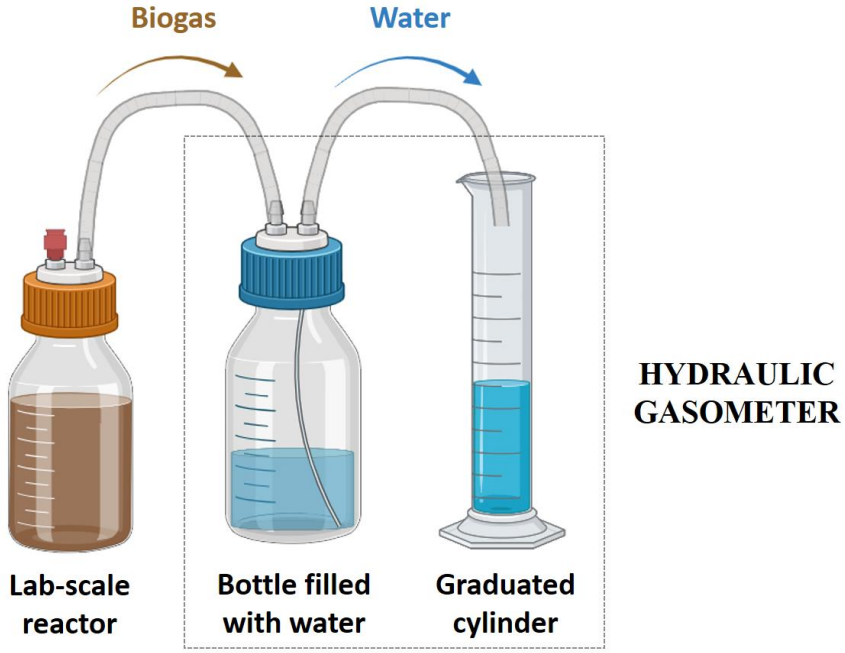

Figure 2. Representation of a laboratory-scale anaerobic digestion reactor connected to a hydraulic gasometer. The quantification of the volume of biogas produced is obtained by measuring the volume of displaced water.

Table 1. Main chemical characteristics of the inoculum [a].

Parameter	Inoculum
Dry matter (%)	19.54 ± 0.81
VS (g/kg)	615 ± 18.4
pH	8.26 ± 0.15
EC (dS/m)	22.66 ± 1.47
TOC (g/kg)	339 ± 11.0
NH_4^+-N (g/kg)	17.64 ± 1.21
FOS/TAC	0.42 ± 0.08

[a] All data expressed on a dry weight basis.

2.4. Analytical Methods

The moisture content was measured by calculating the weight loss after drying the sample in an oven at 105 °C for 24 h. The % of biodegradation was calculated according to the Equation (1) provided by ISO 15985:2014 [39]:

$$\% \text{ Biodegradation} = \frac{mC, g(\text{test}) - mC, g(\text{blank})}{mC, i} \times 100 \quad (1)$$

where $m_{C,g}$ is the amount of gaseous carbon in grams evolved after anaerobic biodegradation, from test (test material) and blank (inoculum), and $m_{C,i}$ is the amount of carbon in grams initially present in the test material. This method allowed for the determination of the biodegradation rate of the tested materials.

The biopolymer biodegradation kinetic of the different biofilms was assessed by fitting biodegradability data to the modified Gompertz model, Equation (2), as described by García-Depraect et al. [44]:

$$C = P \times exp\left\{-exp\left[\frac{R \times e}{P} \times (\lambda - t) + 1\right]\right\} \quad (2)$$

where C represents the cumulative carbon in the gas phase (mg of C per g of bioplastic) at time t (days), P denotes the maximum amount of bioplastic carbon converted to gaseous

carbon (mg of C per g of bioplastic), R is the peak mineralization rate (mg of C per g of bioplastic per day), λ is the delay period (in days) before gas-phase carbon release, and e refers to Euler's number (approximately 2.71828).

Electrical conductivity (EC) and pH were evaluated on fresh material using a benchtop conductivity meter and a benchtop pH meter, respectively. The total volatile solids (VS) content of the digestate was assessed by measuring the weight loss after ashing the sample at 550 °C for 24 h in a muffle furnace. The total organic carbon content used for estimating organic matter (OM) in the digestate was measured utilizing the Springer–Klee wet dichromate oxidation method [45]. Fresh sample was used for the assessment of NH_4^+-N by means of the micro-Kjeldahl distillation method [46]. The FOS/TAC parameter was evaluated as a ratio between the total volatile fatty acids (expressed as mg/L of CH_3COOH equivalent) and alkalinity (expressed as mg/L of $CaCO_3$) [43].

2.5. Statistical Analysis

The analyses performed in this study are presented as mean values of 3 samples ± standard error (SE). Two-way ANOVA Tukey's multiple comparisons test was utilized to determine the significance of the differences in the sample mean values. The standard error of the mean (SEM) was reported. A significance level of $p < 0.05$ was set for the data. All statistical analyses were conducted using GraphPad Prism 9.0.0 for Windows (GraphPad Software, San Diego, CA, USA).

2.6. Life Cycle Assessment (LCA) Analysis

The considered batch scale manufacturing technology is in principle compatible with an industrial scale production (even if the production rate is not comparable): for this reason, the related life cycle inventory (LCI) was built up taking into consideration data coming from industrial processes included in the used software (SimaPro version 9.5.0.1) databases (Ecoinvent 3.9).

2.6.1. Methodology

In this study, the environmental performance of three different biopolymeric film-based systems has been investigated. PLA, PLA_PBS, and PLA_PBS_3CNC films were studied for the whole life cycle, from the extraction and processing of all raw materials to the end-of-life, although the use phase has been neglected as single-use products and no food or other kinds of contaminations have been taken into account.

The waste management phase regards AD, with the possibility to produce energy through the biogas treatment in a co-generation plant, while the possibility of using the final digestate as a soil improver was not considered.

2.6.2. Goal and Scope

The goal and the scope of the study regard the assessment of the potential environmental performance of the above-mentioned systems, also taking into account the related end of life. In particular, the end of life regards the biopolymer-based films' AD with the possibility to exploit the energy potentially obtained through the produced biogas processing in a co-generation plant, avoiding producing the same amount through benchmark routes. For this purpose, through life cycle analysis, this investigation also aimed at assessing the environmental sustainability of the selected end-of-life route, as well as to verify whether AD in a co-generation plant for biogas production could mitigate the environmental burdens rising from the investigated systems' whole life cycle. Regarding the systems' boundaries, all the flows cross the investigated systems from raw materials extraction to film production (to gate). No issues regarding the film service life, performance, or durability were taken into account. On the other hand, all the flows regarding the systems' end-of-life dealing with the related AD were included. The system's expansion was developed to take into account the possibility of exploiting electric energy and heat produced in an average biogas co-generation plant.

2.6.3. Life Cycle Inventory (LCI)

As introduced, the system's expansion has been developed to take into account the possibility of exploiting electric energy and heat produced in an average biogas co-generation plant, avoiding producing the corresponding amount from benchmark sources:

- Electricity, medium voltage {RER} | market group for electricity, medium voltage | cut-off, S;
- Heat, district or industrial, natural gas {Europe without Switzerland} | market for heat, district or industrial, natural gas | cut-off, S.

Regarding the data quality, the PLA-based polyester is included in the databases (Ecoinvent 3.9) of the used software (SimaPro 9.5.0.1). PBS is not included in the software database; thus, the related model was built up from data collected from the literature regarding the industrial production of this kind of polymer. It has to be pointed out that, where not available in the literature (primary data), averaged data were used for energy used in the processes of the related supply chain [13].

For example, the energy needed for liquid systems' mechanical mixing ranges between 0.5 kW/m^3 and 12 kW/m^3 multiplied by the mixing time, on the base of the system viscosity and the mixing rate. A power of 1.00 kW/m^3 is recommended for low-viscosity systems.

Thermal energy spent within high-temperature processes can be deduced by Equation (3):

$$Q = \frac{\Delta T \sum_i^n m_i C p_i + m_i \Delta H_i}{\eta} \quad (3)$$

where ΔT is the temperature gap the reagent is held during the considered stages (65 °C), Cp_i is the specific heat of the i-th reagent, ΔH_i is the enthalpy related to potential phase changes of the i-th reagent, and η is the system efficiency ($0 < \eta < 1$. Average value 0.75).

The energy needed for processes carried out under vacuum can be estimated by means of Equation (4):

$$E = \frac{Q \Delta P t}{eff} \quad (4)$$

where P (Pa) is the applied pressure gap, Q is the vacuum system flow rate, t is the mere pump working time, and *eff* is the system efficiency (average value 0.72).

The production of CNCs was also modeled on the base of averaged data regarding the whole group of processes carried out in the related supply chain [13]. The energy consumed by the involved batch mode processes was calculated on the basis of the corresponding industrial processes. The industrial scaling up also includes the possibility of water and chemical species reuse in multiple cycles. In this example, as a worst scenario, reactive solutions were considered to be eliminated after only two production cycles. The polymer-based films were successfully produced by means of direct extrusion of the granules and the mentioned nanofiller.

As far as the AD of the mentioned films is concerned, it was carried out under thermophilic conditions (52 °C) and substrate mixing by hand. For a more realistic model, to include energy flows regarding substrate mixing and heating, as well as gas purification and desulfurization carried out in a co-generation plant, a framework regarding several industrial plants was taken into account; thus, averaged data were used [47].

As introduced, the system boundaries also include the biogas co-generation plant, where the produced CO_2 is directly abated as biogenic carbon dioxide. Additionally, in a complete plant where AD and the produced biogas from co-digestion are carried out, many sources of internal losses occur. Moreover, the produced thermal and electric energy also depend on the mere methane content in the processed biogas [48]. For this reason, each one of the elaborated systems is characterized by a proper energy yield.

The final digestate is considered as waste, despite the possibility of it potentially being applied as a fertilizer after different treatments. In this framework, the worst scenario was considered; thus, disposal (garden composting) was assumed.

Primary data were used to model the input and the output flows occurring in the AD stage. In particular, direct measurements were taken to evaluate the weight and the nature of the initial substrate (inoculum) and the final digestate, as well as to model the produced biogas, for whom also the mere methane and carbon dioxide weight and volumes were estimated for any investigated film subjected to the AD.

Inoculum was obtained from the OFMSW digestate. For this reason, the related life cycle includes only the (averaged data) transport phase from the collection site to the digestion plant (5 km).

It has to be pointed out that the thermophilic conditions lead to the evaporation of the moisture contained in the digestate during the AD (about 70% of the initial amount), which is released into the environment as water vapor.

As a functional unit, 1.00 kg for any kind of film was taken into account. In Table 2, the inventories related to the whole life cycle of the investigated films are summarized.

Table 2. Life cycle inventories related to the whole life cycle of the investigated systems.

Flow	Unit	PLA Film	PLA_PBS Film	PLA_PBS_3CNC Film
INPUT				
PLA granules	kg	1.00	0.80	7.77×10^{-1}
PBS granules	kg	-	0.20	1.94×10^{-1}
Cellulose NC	kg	-	-	2.91×10^{-2}
Film extrusion	kg	1.00	1.00	1.00
Inoculum transport (Euro 4 lorry, 7.5–16 tons)	tkm	3.41×10^{-1}	3.44×10^{-1}	3.42×10^{-1}
EMISSIONS IN ATMOSPHERE				
Ammonia	kg	1.76×10^{-3}	1.79×10^{-3}	1.78×10^{-3}
NOx	kg	2.69×10^{-4}	2.14×10^{-4}	4.34×10^{-4}
Biogenic CO_2	kg	3.98×10^{-1}	3.43×10^{-1}	6.97×10^{-1}
Methane	kg	2.44×10^{-3}	1.85×10^{-3}	3.76×10^{-3}
Water vapor	kg	37.48	38.81	37.82
OUTPUT/WASTES				
Biowaste garden composting	kg	29.62	28.48	28.54
AVOIDED PRODUCTS				
Heat from natural gas at industrial district	kWh	6.43×10^{-1}	4.83×10^{-1}	9.88×10^{-1}
Electric energy from the grid	kWh	1.05	7.59×10^{-1}	1.56

3. Results and Discussion

3.1. Anaerobic Digestion of Biopolymeric Films

The production of biogas is a key metric in evaluating the efficiency of AD for different substrates. At the end of the test period, the cumulative biogas production for each tested sample was detected as follows: inoculum with 51.86 Nm^3/t of TS, cellulose with 102.91 Nm^3/t of TS, PLA with 39.69 Nm^3/t of TS, PLA_PBS with 33.01 Nm^3/t of TS, and PLA_PBS_3CNC with 59.20 Nm^3/t of TS (Figure 3). The high biogas yield from the cellulose sample confirms its suitability as a benchmark for biodegradability tests. Cellulose, being a pure polysaccharide, is readily degraded by microbial consortia in anaerobic conditions, resulting in high biogas yields. The biogas production from PLA and its blends (PLA_PBS and PLA_PBS_3CNC) was significantly lower than that from cellulose samples and similar to the production provided by the inoculum alone. This aligns with existing literature, wherein pure PLA often shows limited biodegradability due to its crystalline structure and relatively slow hydrolysis rate under anaerobic conditions [40,49,50]. The addition of PBS to PLA (as in PLA_PBS) did not substantially enhance the biogas yield, suggesting that the

blend's overall degradation rate is still inhibited by the presence of PLA. However, the slight increase in biogas production in the PLA_PBS_3CNC sample indicates that the inclusion of CNCs might have enhanced microbial activity or provided additional biodegradable material, albeit to a limited extent. This can also be justified by the chemistry of CNCs that positively impacts the interfacial forces exerted with the PLA and PBS matrix increasing interfacial affinity between PBS and CNCs and reducing PLA crystallization [51,52]. These results therefore highlighted how adding CNCs can mitigate the inhibiting effect of PLA on AD improving biogas production. Furthermore, these findings are consistent with studies in the literature that highlight how adding cellulose nanomaterials can improve the biodegradability efficiency of polymer blends [53].

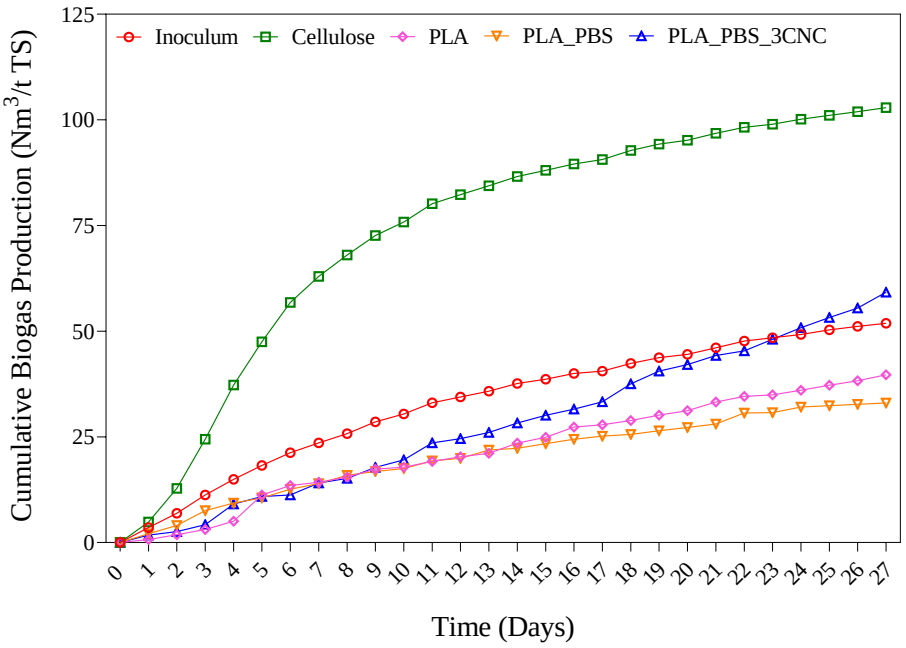

Figure 3. Cumulative biogas production after 27-day thermophilic anaerobic digestion of the sole inoculum, inoculum and cellulose films, inoculum and PLA films, inoculum and PLA/PBS-blended films, and inoculum and PLA/PBS-blended films added with CNCs, expressed as Nm^3 of biogas per ton of total solids (SEM = 5.663).

Engineering the composition of polymer blends could therefore be a possible way forward to increase the biogas yield during AD, as well as co-digestion with other waste biomasses and the application of different pre-treatments [54,55].

The energy content of biogas produced from the AD process is crucial for evaluating the practical applicability of these substrates in renewable energy production. The biogas energy content typically accounts for around 21.6 MJ/Nm^3 [56]. Using this value, the potential energy yields from biogas production after 27 days of AD for each sample can be estimated as reported in Table 3.

Table 3. Estimated energy production after 27-day thermophilic anaerobic digestion of the sole inoculum, inoculum and cellulose films, inoculum and PLA films, inoculum and PLA/PBS-blended films, and inoculum and PLA/PBS-blended films added with CNCs [56].

	Biogas Produced (Nm^3/t of TS)	**Estimated Energy Produced (MJ/t of TS)**
Inoculum	51.86 ± 5.97	1120.15 ± 129.01
Cellulose	102.91 ± 9.44	2222.75 ± 203.97
PLA	39.69 ± 4.26	857.34 ± 91.92
PLA_PBS	33.01 ± 7.20	713.11 ± 155.44
PLA_PBS_3CNC	59.20 ± 5.32	1278.70 ± 114.85

These results indicate that cellulose, as expected, has the highest potential for energy production due to its higher biogas yield. The energy yields from PLA and its blends, although lower, still represent significant renewable energy potential. This is particularly important given the increasing emphasis on sustainable and renewable energy sources. In particular, the presence of PLA blends added with CNCs in AD could contribute to enhancing energy yield and renewable energy production, helping to meet the objectives of a circular economy and sustainable development. These results are in line with what was observed in a previous study on organic waste, where energy production after 1 month was found to be around hundreds of MJ per ton of TS [29].

The mg of gaseous C evolved per gram of TS over 27 days of thermophilic AD for each sample was calculated according to ISO 15985:2014 [39]. The reactors containing cellulose showed a higher carbon yield compared to other samples. In contrast, reactors with PLA biofilms released lower amounts of carbon, with variations depending on the composition. Remarkably, the addition of CNCs to the PLA_PBS blend resulted in a notable increase in carbon output compared to the PLA and PLA_PBS samples, allowing for this blend to overcome the inoculum in the final yield (Table 4). These values represent the cumulative carbon released as CO_2 and CH_4, indicative of the substrates' biodegradability. Cellulose films, representing the positive control, emitted the highest amount of C, standing out as the most easily degradable substrate. PLA and its blends emitted significantly less C, highlighting their slower degradation rates. This aligns with previous studies that reported the challenges in the anaerobic biodegradation of PLA due to its physicochemical properties such as crystalline structure, porosity, and high molecular weight [40,49,50]. The higher C emissions detected from PLA_PBS_3CNC compared to the other PLA-based biofilms suggest that the addition of CNCs enhances the overall biodegradation under the tested conditions. These findings are critical for understanding the environmental impact of using these materials in AD processes. The C emissions data provide indeed insights into the efficiency of the biodegradation process. Higher C emissions detected for cellulose reflect efficient substrate conversion into biogas, while in contrast, the lower emissions observed for PLA and its blends highlight the need for further biofilm optimization or a prolonged anaerobic process to enhance their biodegradability.

Table 4. Initial organic matter and cumulative quantities of mg of gaseous C evolved per g of total solids after 27-day thermophilic anaerobic digestion of the sole inoculum, inoculum and cellulose films, inoculum and PLA films, inoculum and PLA/PBS-blended films, and inoculum and PLA/PBS-blended films added with CNCs, and % of biodegradation of biopolymeric films after 27-day thermophilic anaerobic digestion.

	Initial OM [a] (g DW Basis)	**Cumulative Gaseous C Evolved (mg)**	**Biodegradation of Biopolymeric Films (%)**
Inoculum	8.89 ± 0.29	27.8 ± 3.20	-
Cellulose	9.89	55.1 ± 5.06	93.86
PLA	9.89	21.3 ± 2.28	0
PLA_PBS	9.89	17.7 ± 3.85	0
PLA_PBS_3CNC	9.89	31.7 ± 2.85	31.74

[a] For biopolymers, 1 g of organic matter added to the inoculum was considered.

The percentage of biodegradation of different biofilm samples after 27 days of thermophilic AD shown in Table 4 was also calculated following the ISO 15985:2014 guidelines [39]. The highest % of biodegradation was detected for cellulose, accounting for approximately 93.86%, indicating that cellulose was the most biodegradable sample under the test conditions. For PLA_PBS_3CNC biofilm the biodegradation percentage was significantly lower, i.e., 31.74%, highlighting its slower and less complete degradation, while for PLA and PLA_PBS, the % could not be estimated using the provided equation due to the lower emission of gaseous C compared to the blank represented by the inoculum. These results are in line with what has been found in the literature since the AD of bioplastics, even under thermophilic conditions, rarely reaches high degradation percentages; specifically, to reach an 80% degradation of PLA,

an average of at least 70 days is necessary, while for PBS in thermophilic conditions of AD, no biodegradation was detected after 50 days [57]. This evaluation can provide an estimate of the biodegradability of a polymer, since high percentages represent a good biodegradation degree of the OM. These findings then suggested that cellulose-containing reactors featured both the highest biogas production and biodegradability. On the contrary, reactors containing PLA films or its blends highlighted more inhibited AD process. It is noteworthy that the PLA_PBS_3CNC biofilm was the one with higher biogas production and % of biodegradation compared to the other PLA-made biofilms, suggesting how CNCs could enhance its biodegradability while mitigating environmental impacts.

The anaerobic biodegradability of the biopolymeric films was then evaluated over the tested period in order to compare the different degradation kinetics using the modified Gompertz model [44]. As shown in Figure 4, the cellulose films demonstrated a high biodegradability, reaching 90% of biodegradation after 11 days and a plateau of approximately 93% by day 14, indicative of its suitability as a benchmark for this study following the expected trend for a highly biodegradable material. This behavior aligns with the literature, where cellulose material is consistently reported to undergo efficient breakdown in anaerobic environments due to its polysaccharide structure, which is readily metabolized by anaerobic microorganisms [58]. In contrast, the PLA and PLA_PBS samples exhibited no measurable biodegradation throughout the experimental period, underscoring the inherent resistance of these materials to AD. This finding is consistent with previous studies, which report that PLA, while considered a biodegradable polymer under industrial composting conditions, is resistant to degradation in anaerobic environments due to its crystallinity, molecular weight, porosity, and accessible surface area, which can hinder microbial activity [40,49,50]. Notably, the PLA_PBS_3CNC biofilms displayed a distinct degradation pattern. Although the initial biodegradation of this sample was negligible, it started showing degradation after approximately 20 days, reaching a biodegradation percentage of 31.74% by the end of the experiment. This result suggests that the addition of CNCs to the PLA/PBS blend can significantly enhance the biodegradability of the material under anaerobic conditions. The observed increase in biodegradation of the PLA_PBS_3CNC blend can be attributed to the role of CNCs in improving the structural and functional properties of biopolymers and facilitating the hydrolysis process, as discussed in prior studies [59–61].

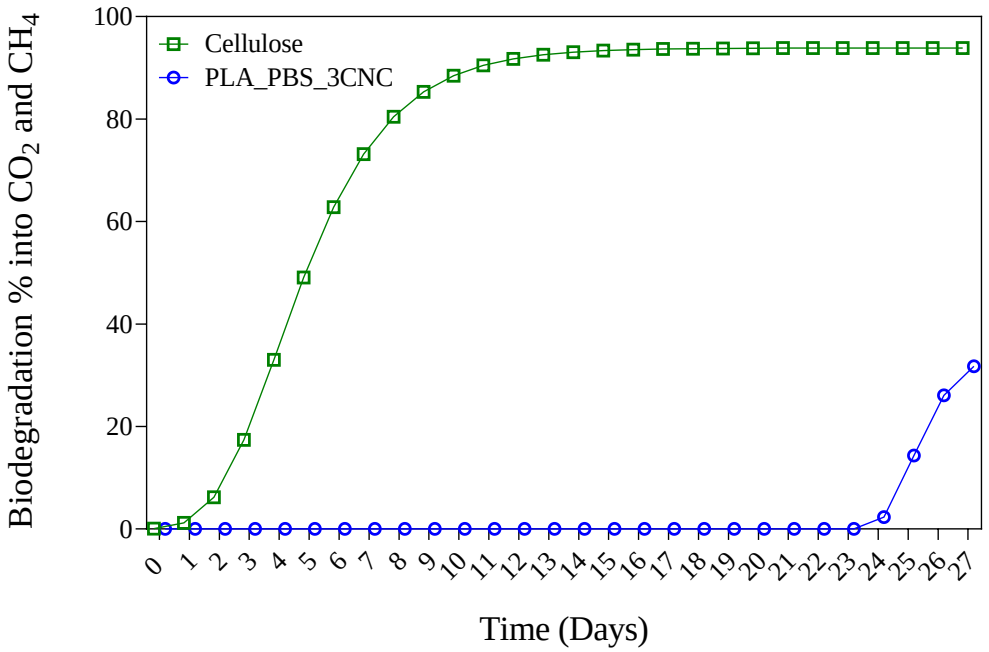

Figure 4. Biodegradation kinetics of biopolymeric films fitted to the modified Gompertz model following 27-day thermophilic anaerobic digestion expressed as biodegradation % into CO_2 and CH_4.

3.2. Environmental Implications of Biopolymer End-of-Life

As previously introduced, the second part of this study focused on LCA and environmental impacts of using different biofilms for AD. SimaPro 9.5.0.1 LCA software was employed, and two main tools were utilized:

- ReCiPe 2016 Endpoint (H): This method addresses a wide range of environmental concerns at the midpoint level and then aggregates the midpoints into a set of three endpoint categories. Endpoint characterization represents a model of the impact on a given effect (i.e., human health, ecosystems, and resources). Midpoint methods measure an effect before the damage to the areas of protection occurs. Endpoint results can be aggregated so that a single score expresses all the impacts that a given product has on the environment;
- ReCiPe 2016 Midpoint (H): this method was used as a tool aimed at the quantification of a wide range of impact categories (midpoint parameters).

Figure 5 summarizes the LCA score, found through the application of the ReCiPe 2016 Endpoint (H), regarding the life cycle of the investigated systems. Due to the use of CNCs, produced through several processing stages, many of them characterized by the use of chemicals and energy-intensive processes (i.e., freeze-drying), the potential environmental impact of the film based on the PLA/PBS blend reinforced with the above-mentioned nanofiller is considerably higher than the other ones. This scenario was obtained without referencing the higher performance of the former system (mechanical, gas barrier properties, and durability), as it is out of the scope of this investigation, where the main focus is attributed to the end-of-life routes of each system.

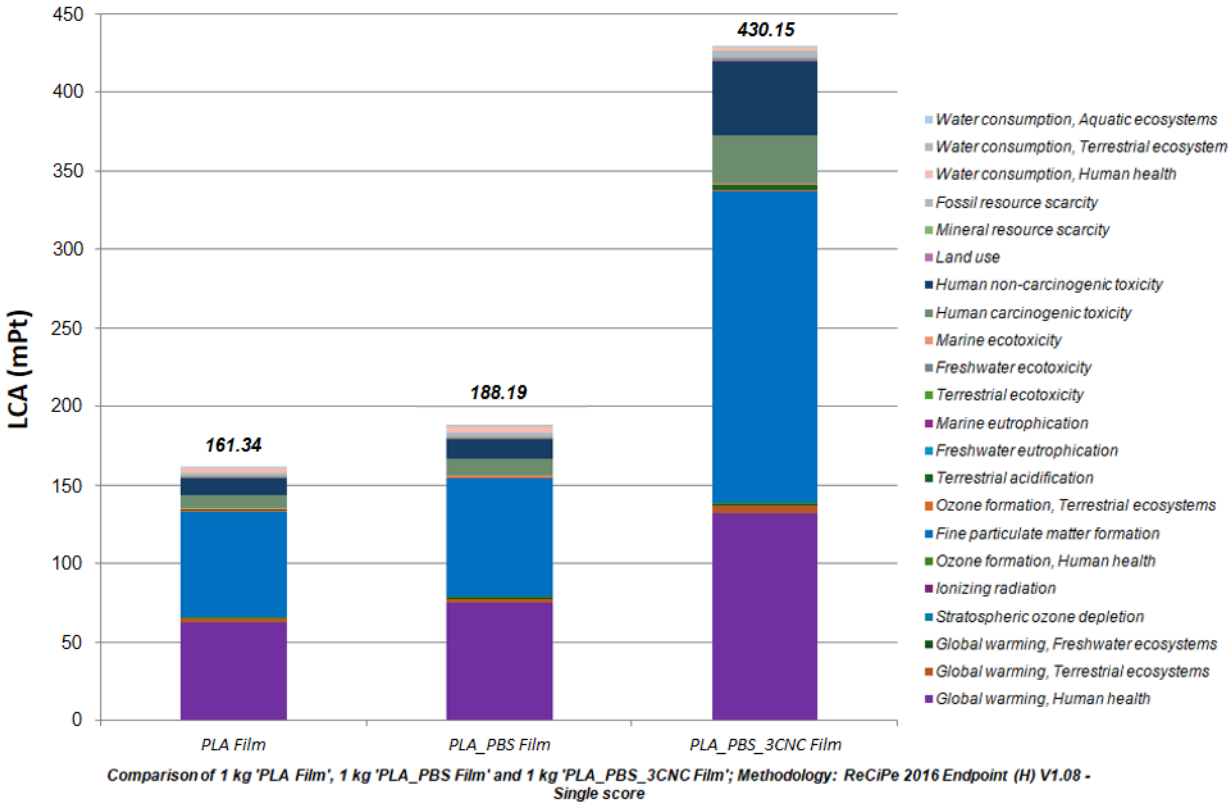

Figure 5. Comparison of the LCA score obtained for the investigated system, analyzed by means of the ReCiPe 2016 Endpoint (H) tool.

The LCA score of the above-mentioned blend is slightly higher than the score of the PLA-based system.

As shown in Figures 6 and 7, the environmental contribution of the end of life for the unfilled systems is negligible, as it potentially represents 1.18% of the total score for the

PLA-based film and 3.33% for the PLA/PBS blend-based one. The investigated route is very interesting, but, because of the low amount of biogas produced, the low energy that can be produced in a co-generation plant, together with the large amount of final digestate to be disposed of, does not thus allow for any relevant mitigation of the environmental burden arising from the related production stages.

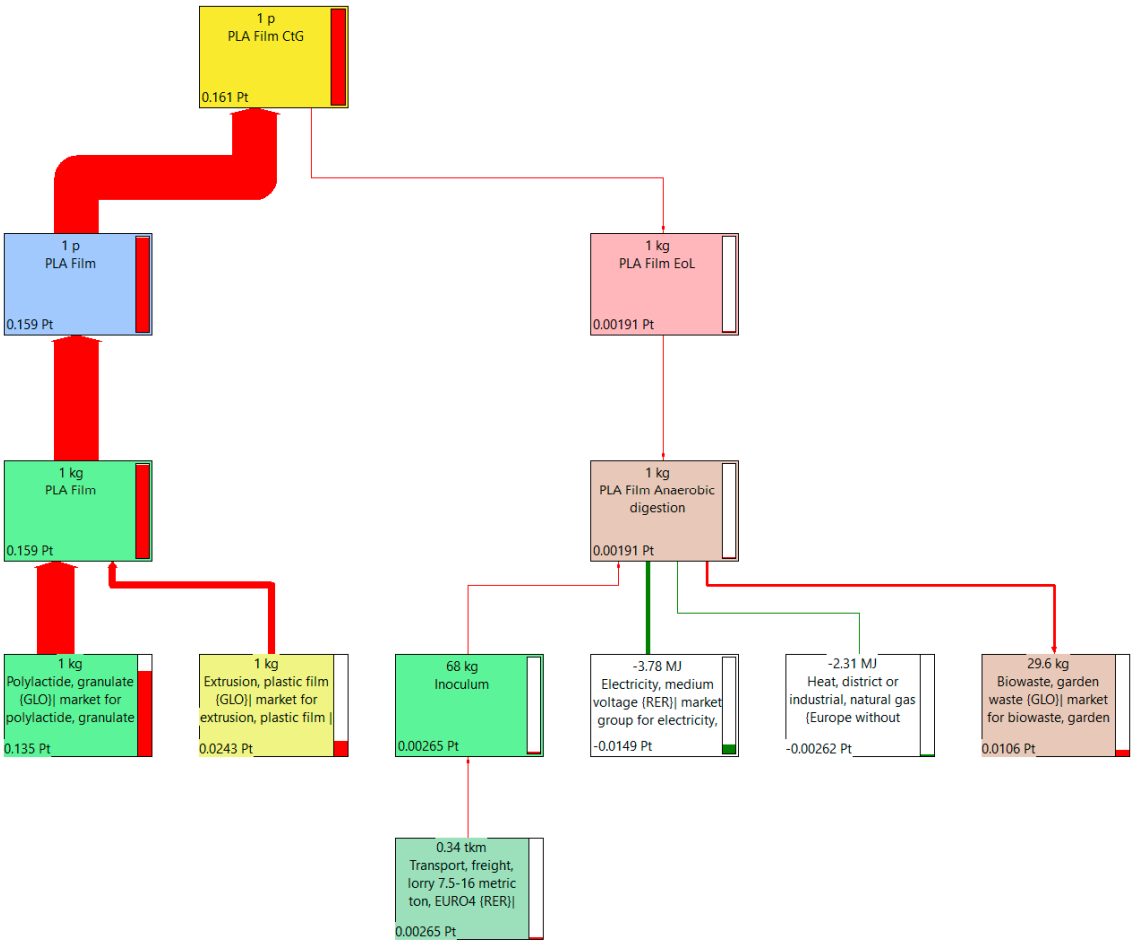

Figure 6. Process tree and LCA score related to the film based on PLA biopolymer. Cut-off 0.50%.

On the other hand, more biogas and energy can be produced in the case of CNC-reinforced PLA/PBS blend AD, compared to the other unfilled systems, which potentially leads to a negative LCA score for the related end-of-life route, and thus a potentially positive environmental impact. Unfortunately, the improvement (mitigation) that can be potentially obtained amounts to only 1.34% (Figure 8).

The described scenario could be considered encouraging, and this route can be preferred to other benchmark end-of-life routes, such as direct composting, incineration, etc., although the performance in terms of biogas production needs to be significantly improved with the aim to increase the sustainability of the investigated systems.

As shown in Figure 8, the production phase is responsible for the whole environmental impact of the biobased polymer films considered. For the PLA and the PLA/PBS blend-based films, the most important flows concern polymer production. For the film reinforced with the CNCs, this nanofiller is responsible for nearly 60% of the whole impact, despite representing less than 3% in weight of the total system, while PLA and PBS granule production contribute 21% and 10%, respectively (PLA represents 80% of the matrix weight as in the unfilled blend, while the PBS represents the remaining 20% of the matrix weight).

Regarding the end-of-life phase, as shown in Figure 8, the positive scenario due to the possibility of using energy from the produced biogas is completely counterbalanced by the negative scenario related to the environmental burdens due to digestate compositing,

inoculum transport and the materials and energy flows crossing the AD plant, as well as the co-generation ones.

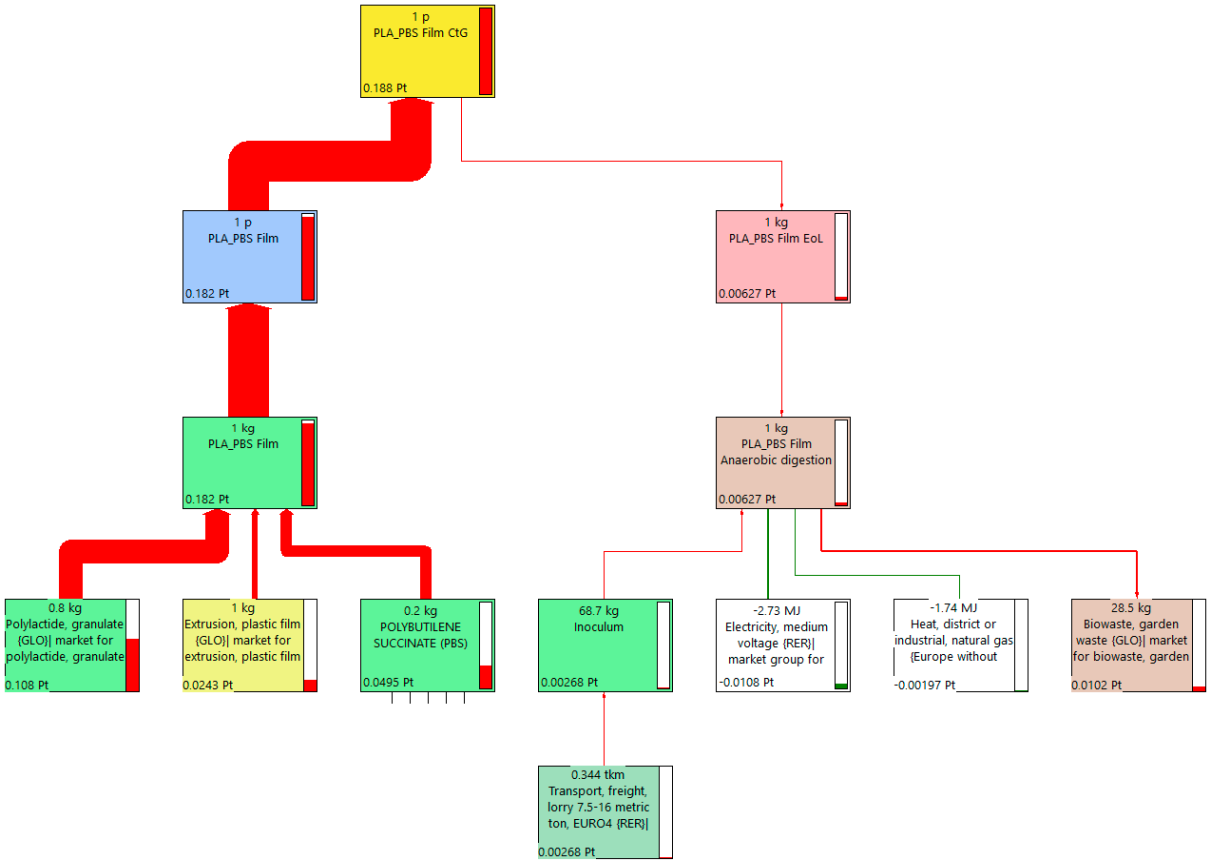

Figure 7. Process tree and LCA score related to the film based on PLA/PBS blend. Cut-off 0.50%.

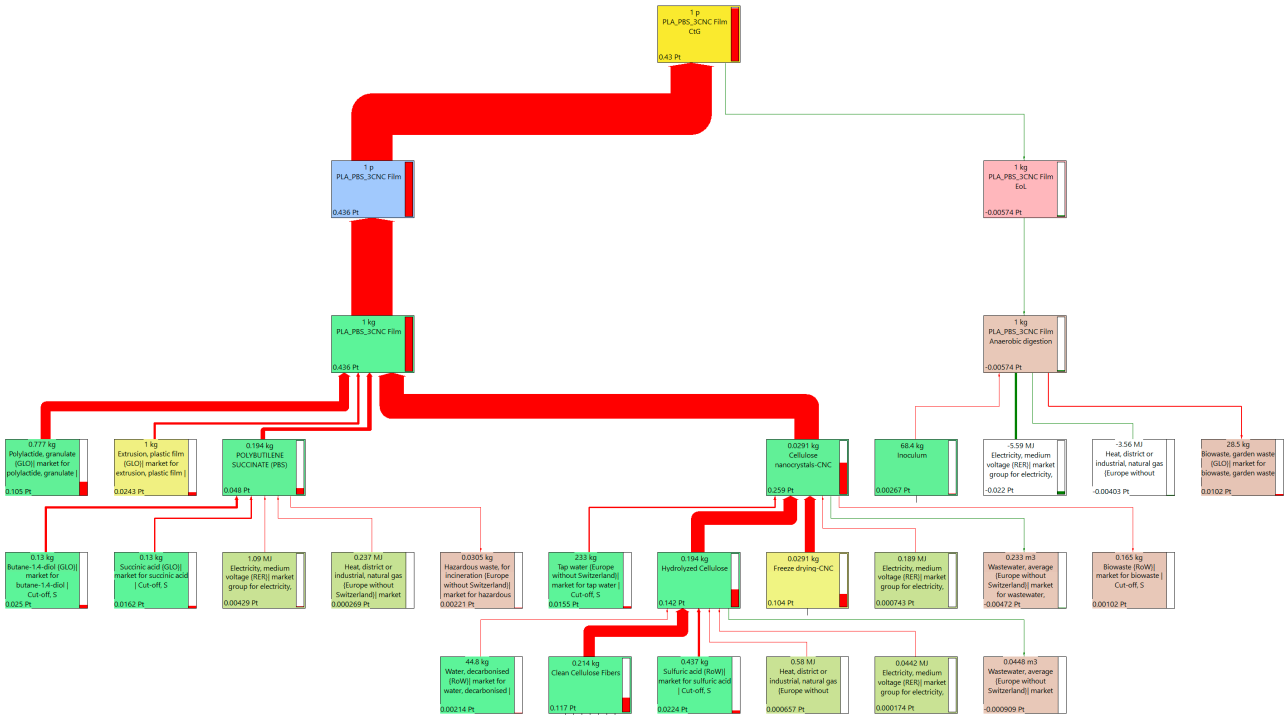

Figure 8. Process tree and LCA score related to the film based on PLA/PBS blend reinforced with CNCs. Cut-off 0.50%.

As shown in Figure 9, the most relevant impact categories in the considered life cycle of the three systems include global warming and fine particulate matter formation, generally caused by energy used to produce the required raw materials and to carry out the processes included within the three kinds of biofilm supply chain. In the case of the unfilled systems, more than 40% of the impact is due to global warming and another 40% to the particulate matter formation. In the case of the filled system, global warming is responsible for 32% of the total impact, while particulate matter formation is responsible for more than 45% of the total impact.

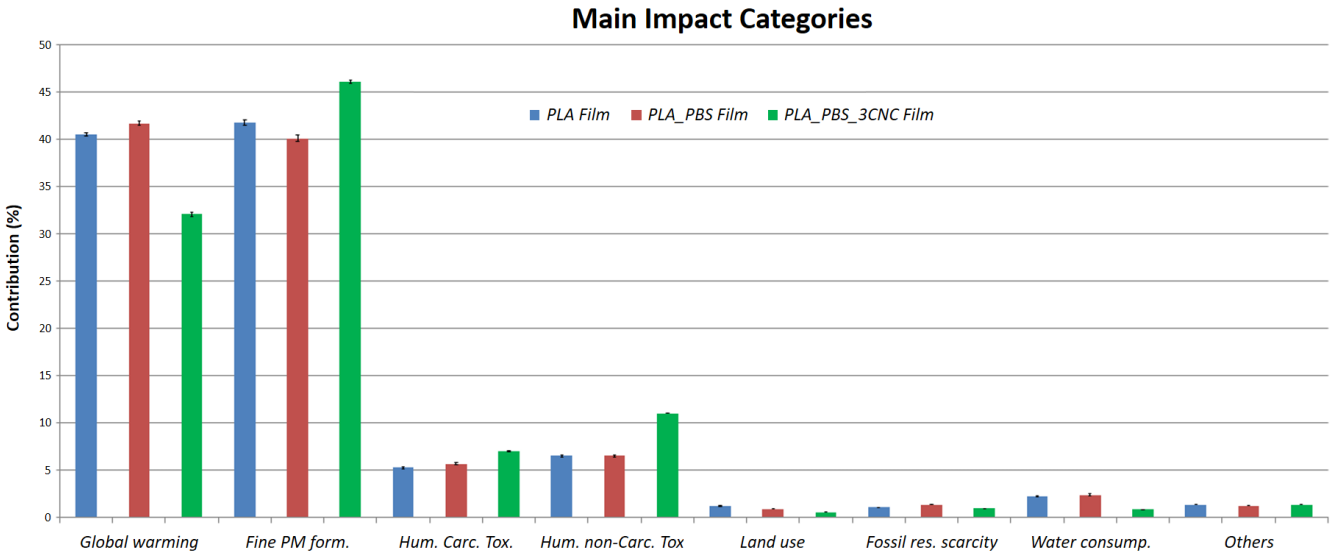

Figure 9. Most important impact categories in the case of the investigated systems.

Another 10% of the total LCA score is due to human toxicity generated by the emission of carcinogenic and non-carcinogenic substances. The related contribution is higher in the case of the reinforced film (about 17%). A less significant role is played by the whole range of the other impact categories, such as land use, fossil and mineral resource exploitation, and water consumption.

The aforementioned impact categories have been measured through the quantification of the corresponding impact indicators, as summarized in Table 5.

Table 5. Quantification of the impact indicators related to the investigated systems.

Impact Category	Unit	PLA Film	PLA_PBS Film	PLA_PBS_3CNC Film
Global warming	kg CO_2 eq	4.03	4.83	8.51
Stratospheric ozone depletion	kg CFC11 eq	2.83×10^{-5}	2.68×10^{-5}	2.93×10^{-5}
Ionizing radiation	kBq Co-60 eq	4.27×10^{-2}	0.20	1.62
Ozone formation, human health	kg NO_x eq	9.58×10^{-3}	1.07×10^{-2}	1.90×10^{-2}
Fine particulate matter formation	kg $PM_{2.5}$ eq	6.43×10^{-3}	7.20×10^{-3}	1.89×10^{-2}
Ozone formation, terrestrial ecosystems	kg NO_x eq	1.02×10^{-2}	1.14×10^{-2}	2.01×10^{-2}
Terrestrial acidification	kg SO_2 eq	1.86×10^{-2}	2.01×10^{-2}	5.34×10^{-2}
Freshwater eutrophication	kg P eq	1.45×10^{-3}	1.67×10^{-3}	5.53×10^{-3}
Marine eutrophication	kg N eq	1.43×10^{-3}	1.19×10^{-3}	3.19×10^{-3}
Terrestrial ecotoxicity	kg 1.4-DCB	12.99	14.32	46.76
Freshwater ecotoxicity	kg 1.4-DCB	0.16	0.17	0.65
Marine ecotoxicity	kg 1.4-DCB	0.20	0.21	0.84

Table 5. *Cont.*

Impact Category	Unit	PLA Film	PLA_PBS Film	PLA_PBS_3CNC Film
Human carcinogenic toxicity	kg 1.4-DCB	0.15	0.19	0.55
Human non-carcinogenic toxicity	kg 1.4-DCB	2.76	3.24	12.47
Land use	m^2a crop eq	0.82	0.72	1.04
Mineral resource scarcity	kg Cu eq	1.05×10^{-2}	1.14×10^{-2}	3.54×10^{-2}
Fossil resource scarcity	kg oil eq	0.84	1.19	2.15
Water consumption	m^3	0.15	0.17	0.20

Table 6 summarizes the contribution of the end-of-life route to each indicator's value for the entire group of investigated systems. It can be seen that the end-of-life route for the above-mentioned systems contributes to lowering the value of most impact indicators. The problem is that this decrease does not occur for the most important indicators, such as global warming and fine particulate matter formation. A slight decrease (lower than 0.50%) occurs only in the case of the system based on the nano-reinforced film.

Table 6. Contribution of the end-of-life (EoL) phase to the impact indicator's value for the investigated systems.

Impact Category	Contribution of the EoL Route (%)		
	PLA Film	PLA_PBS Film	PLA_PBS_3CNC Film
Global warming	+4.69	+5.96	−0.37
Stratospheric ozone depletion	+61.40	+62.40	+56.77
Ionizing radiation	−516.82	−78.11	−20.17
Ozone formation, human health	−0.79	+0.74	−1.53
Fine particulate matter formation	+1.97	+4.03	−0.47
Ozone formation, terrestrial ecosystems	−0.29	+1.17	−1.33
Terrestrial acidification	+18.51	+19.74	+5.68
Freshwater eutrophication	−22.89	−14.26	−8.90
Marine eutrophication	−1.61	−1.34	−1.10
Terrestrial ecotoxicity	+3.75	+4.62	+0.45
Freshwater ecotoxicity	−8.87	−5.70	−3.29
Marine ecotoxicity	−9.07	−5.63	−3.31
Human carcinogenic toxicity	−14.49	−7.75	−6.39
Human non-carcinogenic toxicity	−14.47	−8.43	−4.96
Land use	+14.61	+16.43	+10.58
Mineral resource scarcity	−4.98	−2.85	−2.45
Fossil resource scarcity	−11.07	−4.60	−7.90
Water consumption	−2.55	−1.48	−3.96

This further demonstrates that the end-of-life phase for PLA and PLA/PBS blend does not worsen their environmental impact but, at the same time, does not produce any significant mitigation of their environmental impact arising from the related life cycle up to the production stage (cradle-to-gate). Actually, a slight improvement occurs due to the end-of-life route for the PLA/PBS-based film reinforced with CNCs, despite the very low amount.

As shown in Figure 10, the most important environmental effect throughout the whole life cycle of the investigated films concerns human health, which is responsible for nearly the entire related impact. Considerably less relevance concerns the ecosystem quality and abiotic resource exploitation.

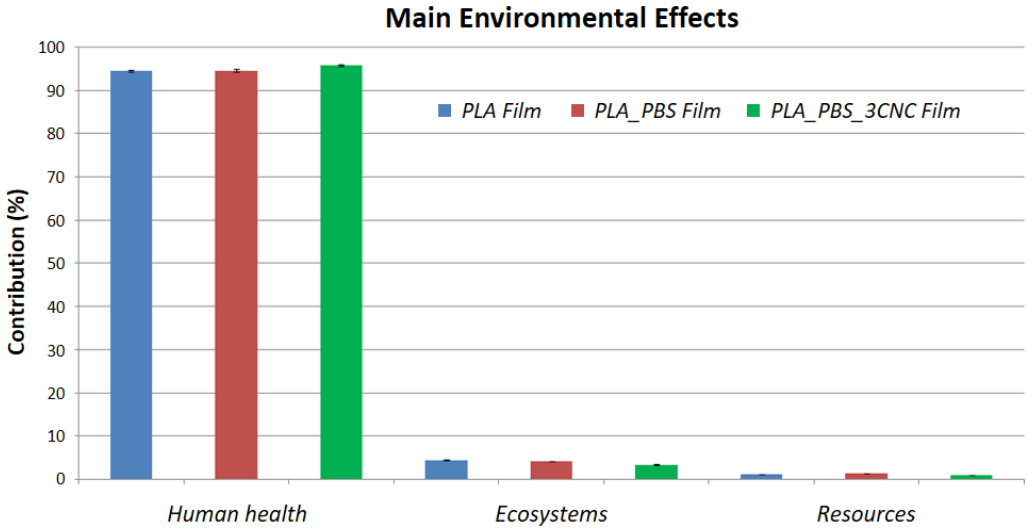

Figure 10. Most important environmental burdens in the case of the investigated systems.

Figures 9 and 10 show that the standard error, related to the contribution, respectively, of each single impact category and environmental burdens to the investigated film environmental impact, is very low, as the end-of-life phase for the above-mentioned systems with respect to the corresponding life cycle does not significantly affect the LCA score (it actually seems to be nearly negligible). Therefore, the changes in the produced biogas in comparison to the measured average value produce small variations in the whole LCA score, and also in the impact indicators and environmental burdens.

Table 7 summarizes the quantification of the main environmental damages related to the whole life cycle of the PLA-based film, the PLA/PBS blend-based one, and the latter blend reinforced with the CNC system. For the unfilled films, the end-of-life contributes to a slight increase in issues such as human health and ecosystem quality, as shown also in Table 8. On the other hand, the end-of-life contributes to decreasing resource exploitation. In the case of the nanocomposite film, the end-of-life contributes also to slightly decreasing human health issues.

Table 7. Quantification of the environmental damages related to the investigated systems.

Damage Category	Unit	PLA Film	PLA_PBS Film	PLA_PBS_3CNC Film
Human health	DALY	9.14×10^{-6}	1.07×10^{-5}	2.47×10^{-5}
Ecosystems	Species × yr	2.63×10^{-8}	2.86×10^{-8}	5.30×10^{-8}
Resources	USD2013	0.24	0.36	0.58

Table 8. Contribution of the end-of-life (EoL) phase to the environmental damage value for the investigated systems.

Damage Category	Contribution of the EoL Route (%)		
	PLA Film	PLA_PBS Film	PLA_PBS_3CNC Film
Human health	+1.01	+3.20	−1.39
Ecosystems	+7.85	+8.88	+2.10
Resources	−11.01	−4.58	−7.83

4. Conclusions

The biogas production from various substrates after about one month highlighted significant differences in anaerobic digestion efficiency. Cellulose biofilms demonstrated the highest biogas production, whereas bioplastics such as PLA and its blends (PLA_PBS and PLA_PBS_3CNC) exhibited lower biogas yields, consistent with the already available literature on PLA's reduced biodegradability during digestion. The inclusion of 3% of cellulose nanocrystals (CNCs) in PLA_PBS_3CNC slightly improved biogas output, suggesting enhanced biodegradation of this blend. The estimated energy content of biogas reflected cellulose's superior potential for energy production, while PLA and its blends offered modest yet notable renewable energy contributions, with PLA_PBS_3CNC blend yielding higher values compared to the other PLA-made biofilms. The % of biodegradation for cellulose after the tested period accounted for approximately 93.86% followed by PLA_PBS_3CNC biofilm with 31.74%, highlighting how CNCs can markedly enhance the biodegradability of PLA/PBS blends and play a critical role in promoting the anaerobic degradation of biopolymer blends, although a longer digestion time is probably needed to achieve greater biodegradation. On the contrary, PLA and PLA_PBS blends showed no degradation, highlighting the limitations of these materials under the tested conditions.

In this investigation, the LCA of three biofilm systems was also carried out according to a "Cradle-to-Gate" approach. The end-of-life stage regards anaerobic digestion aimed at the production of energy in a co-generation plant. This scenario allows for avoiding the production of the same amount of (electric and thermal) energy. On the other hand, the resulting digestate has been assumed as subjected to composting.

Despite the end-of-life route diverting the biofilms from landfilling, incineration, and mainly from direct industrial composting, the amount of produced biogas is very low, as well as the energy potentially produced. For this reason, this disposal route cannot be considered as a mitigation action of the environmental effects related to the whole life cycle of the investigated biodegradable films. Only in the case of the system reinforced with CNCs does the end-of-life slightly mitigate the environmental burdens related to the other stages of the biofilm life cycle, as a consequence of the higher amount of produced biogas.

However, for the management of biodegradable wastes diverted from direct industrial composting, anaerobic digestion appears as an environmentally favorable option, as a consequence of the conversion of organic waste into biogas, which is a renewable energy source. Overall, these findings emphasize the potential for optimizing bioplastic blends, particularly with CNCs, to enhance biodegradability and renewable energy production. Anyway, more sustainable scenarios have to be investigated for biopolymer-based food packaging as a further milestone toward a circular economy, including optimizing anaerobic digestion conditions for enhanced biodegradability and biogas production. Future studies could investigate process improvements evaluating anaerobic digestion efficiency in different operating conditions. The effectiveness of applying different pre-treatments along with the co-digestion with other biomass types could be further investigated to maximize the biogas yield potential of different biopolymeric blends.

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