energies

Article

Multi-Criteria Analysis of the Influence of Lignocellulosic Biomass Pretreatment Techniques on Methane Production

Magdalena Zdeb [1], Marta Bis [1,*] and Artur Przywara [2,*]

[1] Faculty of Environmental Engineering, Lublin University of Technology, Nadbystrzycka 40B, 20-618 Lublin, Poland
[2] Faculty of Production Engineering, Department of Machinery Exploitation and Management of Production Processes, University of Life Sciences, Głęboka 28, 20-612 Lublin, Poland
* Correspondence: m.bis@pollub.pl (M.B.); artur.przywara@up.lublin.pl (A.P.)

Abstract: Methane from environmentally friendly anaerobic digestion may be an alternative non-renewable source that is depleting. One of the substrates for that process may be lignocellulose-based materials. The article concerns comparing the environmental impact as well as technical and energy indicators of alternative ways of producing methane from the anaerobic digestion of *Pennisetum hybrid*. Five scenarios were analyzed: methane production from the anaerobic digestion of the raw grass, the grass subjected to alkaline pretreatment (with 2% NaOH solution at two temperatures), and the grass subjected to mechanical pretreatment (ground to obtain particle sizes <0.18 mm and 0.25–0.38 mm). Multi-criteria decision (MCA) analysis was carried out with the use of five indicators, including life cycle assessment results as well as methane production parameters, in order to optimize this sustainable way of bioenergy production. The purpose of this study was to identify the most cost-effective and environmentally friendly method of *Pennisetum hybrid* pretreatment in order to optimize the methane production process in terms of environmental, technical, and economic aspects. According to the obtained results, it was stated that the most advantageous solution for the majority of the analyzed indicators turned out to be the mechanical pretreatment with grinding the lignocellulosic biomass into a particle size <0.18 mm.

Keywords: bioenergy; lignocellulosic biomass pretreatment; *Pennisetum hybrid*; methane production; anaerobic digestion; multi-criteria analysis; life cycle assessment; global warming potential; cumulative energy demand; IMPACT 2002+

Citation: Zdeb, M.; Bis, M.; Przywara, A. Multi-Criteria Analysis of the Influence of Lignocellulosic Biomass Pretreatment Techniques on Methane Production. *Energies* **2023**, *16*, 468. https://doi.org/10.3390/en16010468

Academic Editors: Panagiotis Tsapekos and Merlin Alvarado-Morales

Received: 19 November 2022
Revised: 20 December 2022
Accepted: 27 December 2022
Published: 1 January 2023

1. Introduction

The activity of burning fossil fuels, such as hard coal, natural gas, or crude oil, for energy production causes the depletion of these natural resources and environmental contamination, especially through the emission of greenhouse gases. Therefore, it is necessary to look for other energy carriers. Nowadays, more and more attention is paid to renewable sources. The biogas produced in anaerobic digestion (AD), which contains 45–70% methane, may be an alternative source of energy, as it can be used for electricity and heat production and as vehicular fuel [1]. Among many AD feedstocks, lignocellulosic materials, often considered waste, are regarded as a substrate with a high potential biogas yield and a carbon-zero footprint [2]. Moreover, they are cheap and widely available [3,4]. Their global yield amounts to about 1.3 billion tons every year [5]. Lignocellulose-based materials are characteristic because of the complex structure of a large number of cross-linked polysaccharide networks, glycosylated proteins, and lignin [6]. The polymeric structure of these materials, which makes them resistant to enzymatic degradation, is the main barrier to using them for biofuel production via biological means [7]. One of the lignocellulosic substrates is *Pennisetum hybrid*, a grass characterized by non-food status, rapid growth, high biomass yields, extensive adaptability, and low plantation expenditure [8,9].

The methods of pretreatment are aimed at changing the physical and chemical properties of the lignocellulose-based substrates' recalcitrant structure. They result in increasing the accessibility of lignocellulosic biomass, which enables microorganisms to utilize it in anaerobic digestion. In addition, pretreatment methods can be divided into physical, chemical, and biological [10–12]. The physical pretreatment includes mechanical comminution, extrusion, and ultrasonic pretreatment [13,14]. One of the methods, mechanical pretreatment, concerns particle size reduction and the accessible surface area increase, which results in degradation of the cellulose crystal structure [15,16]. The main advantages of this method are its minimal energy requirements and lack of byproduct formation [17]. Chemical pretreatment involves the addition of chemical compounds, e.g., hydroxides of sodium, potassium, and calcium, ammonium, sulfuric acid, hydrochloric acid, or phosphoric acid [13,18]. Its advantages, besides low costs, are high rates and better efficiencies of complex organic material degradation in comparison to other pretreatment methods [19]. It was proven that alkaline pretreatment effectively removes hemicellulose and lignin from lignocellulosic substrates and increases methane production [20]. Moreover, it is more efficient in energy terms compared to the process conducted in an acidic environment [21]. Generally, pretreatment methods are regarded as the major factors contributing to the high cost of biomass processing; thus, recognition of the lowest-cost variant is of high importance. Several interesting literature reviews summarizing various methods of pretreatment of lignocellulosic biomass have been published, indicating the advantages and disadvantages of each method as well as their costs [22–24].

In addition to the strictly technical or economic approach, the environmental approach has been strongly developing in recent decades (much attention has been paid to the assessment of the environmental impact of individual technologies or processes). Life Cycle Assessment (LCA) is a tool for assessing the environmental impact of a product, process, or activity over the entire period of its life: from production, through use, to disposal or recycling [25,26]. Its advantages, in comparison to other environmental assessment techniques, are the possibility of material and substance flow analysis [27], standardized methodology for each step, and the possibility of obtaining reproducible results [28]. In the case of the lignocellulosic biomass pretreatment processes, this tool enables the assessment of aspects such as energy and resource consumption (water, fossil fuels), as well as emissions to air or water (e.g., greenhouse gases). A significant number of studies in which the environmental impact of bioethanol produced from lignocellulosic biomass (grass, corn stover, wood chips, poplar biomass, sweet sorghum, willow, sugarcane bagasse, herbaceous crops, and forest biomass) was assessed have been published in the literature [29–32]. Different degrees of greenhouse gas (GHG) emissions and fossil fuel use reduction compared to conventional energy use (such as gasoline) were shown. González-García et al. [33] assessed the environmental impact of willow chips as raw material for two different energy uses: ethanol production and its combustion, either in a flexible fuel vehicle—after blending with gasoline—or directly in an industrial furnace for heat production. Some authors studied the environmental impacts of the production of sugars and bio-chemicals from wood-based material in order to compare it with the fossil-based one [34–38]. Several studies concerned the LCA of lignocellulosic biomass pretreatment methods. Chuetor et al. [39] used a combined method of sugarcane bagasse pretreatment (mechanical treatment, chemical treatment, and enzymatic hydrolysis). In this study, the main criterion for selecting the most advantageous method was the energy efficiency of the process and the amount of waste generated. Additionally, part of the research has focused on the pretreatment process in bioethanol production by analyzing various impact criteria. Kumar and Murthy [40] compared steam explosion, hot water, dilute alkali, and dilute acid pretreatments of rice straw in terms of the impact of fossil energy use and GHG emissions. A similar assessment concerning corn stover was conducted by Prasad et al. [41]. They analyzed the impact of such criteria as CO_2 emissions, eutrophication potentials, water depletion, and acidification potential. Four methods of chemical pretreatment of switchgrass using sodium hydroxide, ammonia, methanol, and sulfuric acid were analyzed by Smullen et al. [42]. Interesting research on many environmental and economic indicators was presented by Van Fan et al. [43], who carried out an assessment of physical, chemical, and biological pretreatment methods for lignocellulosic biomass.

While LCA is a good tool to analyze individual impact indicators, it is focused mostly on environmental burdens. The scope of the LCA-based analysis can be extended by using various tools, such as multi-criteria analysis (MCA). Multi-criteria analysis is one of the widely recognized instruments for collecting detailed information on selected aspects, which can be combined with LCA approaches to solve complex problems in a structured and easy manner. The main goal of MCA is to simplify the common presentation of results by expressing all calculated indicators as a percentage of the maximum value obtained [44]. The MCA method has already been used for the evaluation of various biofuels, such as biogas, bioethanol, and biodiesel [45], as well as for the analysis of the technical criteria of lignocellulose-based materials pretreatment [46]. However, there is a lack of broad information on MCA results combining the technical, environmental, and economic aspects of biogas production methods from lignocellulosic substrate in a potentially useful manner. Thus, in this work, MCA will be used to obtain a broader perspective and combine the technical aspects of lignocellulosic biomass pretreatment with environmental considerations.

Therefore, the purpose of this study was to identify the most cost-effective and environmentally friendly method of *Pennisetum hybrid* pretreatment in order to optimize the methane production process in terms of environmental, technical, and economic aspects. The final results of the study will show which scenario of methane production from lignocellulosic biomass is most advantageous in terms of various analyzed parameters and will provide useful information to decision-makers.

2. Materials and Methods

2.1. System Description

Five scenarios based on literature data comparing various pathways of *Pennisetum hybrid* pretreatment before anaerobic digestion were modeled. These scenarios are presented in Figure 1. Each process encompassed a life cycle, from harvesting, through transport, pretreatment, and methane production in the anaerobic digestion process.

The first of the analyzed scenarios (S1) covered only mechanical pretreatment divided into two stages: cutting into 2–3 cm pieces and smashing in a pulverizer for 1 min. to a particle size of 0.38–0.83 mm. The next two scenarios included, in addition to pre-cutting into 2–3 cm pieces, a grinding step on a grinder to sizes 0.25–0.38 mm (S2) and <0.18 mm (S3). Two further scenarios relate to alkaline pretreatment with NaOH. In the S4 scenario, after grinding into 2–3 cm pieces and smashing in a pulverizer, an alkaline treatment was carried out with a 2% NaOH solution. The sample was placed for 24 h in a thermostatic bath at 35 °C. This was followed by cooling in ice at room temperature and then adjusting the pH to 7.0 with HCl solution. In contrast, in the S5 scenario, the alkaline treatment involved a treatment with a 2% NaOH solution at 121 °C in an autoclave for 1 h. The last step in all presented scenarios was anaerobic digestion conducted at 37 ± 0.5 °C for 30 days.

S1, S4, and S5 scenarios (Figure 1) remained similar to those considered by Kang et al. [9], while the S2 and S3 scenarios were analogous to the pretreatment methods presented by Kang et al. [47]. The raw material was a *Pennisetum hybrid* (*P. americanum* × *P. purpureum*). It contained 29.65% of total solids (TS), 26.03% of volatile solids (VS), 40.91% of carbon (C), and 1.05% of nitrogen (N). The contents of cellulose, hemicellulose, lignin, and ash were as follows: 33.9%, 20.7%, 18.4%, and 4.0%, respectively. The inoculum used in the experiments conducted by the above-mentioned authors was taken from a mesophilic continuously stirred tank reactor (CSTR) fed with grass and glucose. It was characterized by a TS content of 6.0%, a VS content of 1.0%, and a pH value of 7.61. Energy efficiency was the criterion for selecting the presented scenarios. In the study by Kang et al. [47] the effect of mechanical treatment on particle composition and anaerobic digestion performance was investigated.

From the analyzed particle sizes, two ranges that gave the best results in terms of methane production efficiency were selected. Similarly, from the work of Kang et al. [9], the aim of which was to optimize the alkaline pretreatment of *Pennisetum hybrid*, two treatment variants with the best results in terms of methane yield and number of days to reach 80% of the methane volume were selected. Additionally, the control variant with raw material without alkaline pretreatment from the second cited work was adopted for analysis.

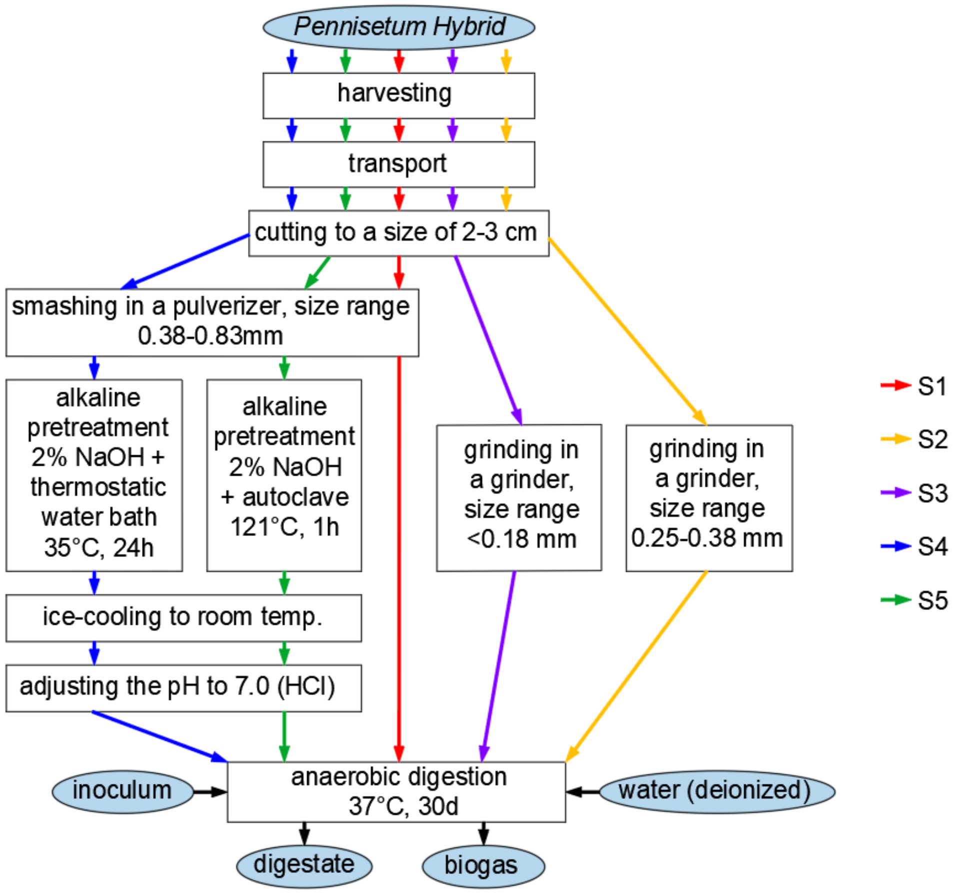

Figure 1. Schematic view of the analyzed processes of pretreatment and anaerobic digestion of *Pennisetum hybrid*.

The biomethane potential (BMP) yields, as well as T_{80} values, were taken from the data presented in detail in the works of Kang et al. [9] and Kang et al. [47]. The BMP values obtained in particular scenarios from S1 to S5, in ml CH_4 gVS^{-1}, were equal to 249.3 ± 12.5, 291.9 ± 4.7, 290.2 ± 4.3, 301.7 ± 9.6 and 271.1 ± 3.9, respectively.

The data on the electricity consumption of the devices were measured in the laboratory of the Faculty of Environmental Engineering of the Lublin University of Technology (Poland) using the Voltcraft Energy Logger 4000 F (Germany). The following devices were used in the study: the Sanyo Electric MLS- 3750 autoclave (Japan), intended for the sterilization of laboratory instruments and glassware, as well as culture media incubation and sample heating; Retsch GmbH, SM300 Cutting Mill (Germany), used for the grinding of tough, medium-hard, soft, elastic, fibrous, and heterogeneous mixes of products; and the BioReactor Simulator (BRS), Bioprocess Control Sweden AB (Sweden), used for the control and monitoring of anaerobic digestion processes in a continuous mode of operation, controlled by a web-based software running on a remote cloud solution.

The authors of this work carried out estimations and measurements of the energy consumption of devices used in these processes, as well as built the analyzed life cycle scenarios and conducted their assessment. The data concerning methane production was taken from the literature.

2.2. Methods of Environmental, Technical, and Economic Criteria Assessment

Multi-criteria analysis pays attention to the multi-purpose and multi-aspect nature of optimized solutions. It seems advisable to use forms of criteria that are distinguished by a clear economic sense, such as unit cost or annual cost, general effect, environmental burdens, etc. However, the selection of the criterion depends on a given, specific decision situation. In ecological and energy analyses, many criteria are most often used in the area of consumption of natural resources and the amount of generated loads (pollutants) to the environment.

A life cycle assessment according to ISO 14040 was conducted in this study to estimate environmental burdens related to the methane production in the analyzed processes. SimaPro v7.2 was used as a tool for LCA performance (PRé Sustainability, The Netherlands). The main functional unit used in this study is 1 dm^3 of produced methane, which refers to the energy output of various processes analyzed while taking into account the differences in biomethane potential yield. The inventory was based on the unit processes, including the substrates and energy needs necessary for a single laboratory bioreactor BRS operation, including the BMP values mentioned in the previous chapter. Energy inputs measured as electricity used by laboratory equipment were replaced in the life-cycle inventory model by energy from biogas to avoid overestimation of environmental burdens in relation to standard industrial procedures. Moreover, the energy needs of equipment were related to its total possible load, so the balance more closely corresponded to real life than laboratory conditions. The data used in the inventory stage was based on my own measurements and calculations related to the energy consumption of particular equipment and material balance, including chemical substrates. These data could be treated as first-class, while another information, such as harvesting, comes from the literature and Ecoinvent v.3 database and can be classified as class three. On the basis of life cycle impact assessment methods, three environmental criteria were applied in this study. The first environmental parameter is cumulative energy demand (CED), which is one of the most popular methods for assessing the efficiency of energy production processes. It can also be used as a proxy indicator for other environmental consequences [48]. Its use enables one to calculate life cycle-based energy production in relation to the energy consumption needed to produce it [49]. In this method, the energy inputs (primary energy from renewable and nonrenewable sources) as well as energy flows for energy and material purposes are analyzed [50,51]. Results are presented as MJ of embodied energy.

Taking into account the occurring and projected climate changes, the global warming potential method in a 100-year perspective (GWP 100a) was used as the second environmental criterion (IPCC 2013). This indicator shows how much energy will be absorbed by 1 ton of an emitted gas over 100 years in comparison to the amount of energy absorbed by 1 ton of carbon dioxide (CO_2) released into the atmosphere [52]. All emissions with a predicted negative impact on the climate balance are converted to the equivalent amount of CO_2 the similar global warming potential ($kg_{CO2eq}/kg_{emission}$) [53].

The IMPACT 2002+ method was used as the third environmental criterion (IMPACT). It proposes a practicable implementation of a combination midpoint/damage approach that links all types of lifecycle inventory results via fourteen midpoint categories. These categories are then classified into four types of end-points (damage categories) facilitating optimization: human health, climate change, ecosystem quality, and resources [54]. Impact 2002+ emphasizes the impact of the analyzed factor on climate change and global warming, in particular with regard to greenhouse gas emissions from energy use [55]. Generally, a higher value of this parameter means a more intense environmental impact, expressed as Pt.

The final results were validated by the Monte Carlo statistical simulations (lognormal distribution and 95% confidence interval), which were implemented in order to analyze the possible error in the obtained results.

Additional criteria for analysis included a technical digestion time, T_{80}. T_{80} is defined as the number of days of the anaerobic process needed to attain 80% of methane volume.

This parameter was chosen due to its importance for possible time reduction, which can be related to achievable energy savings in the anaerobic digestion stage.

The economy of selected methods of methane production is one of the most important issues for potential investors. The calculation of the costs of methane production was based on the measured energy consumption in the assessed processes as well as the necessary chemicals in Scenarios 4 and 5. The price of energy (0.055 EUR/kWh) was based on the European Biogas Association [56].

Considering the results of the multi-criteria analysis, the best option in the case of all indicators is the one with the lowest value.

2.3. The Weighted Sum Method (WSM) as a Method of Multi-Criteria Analysis

There are various mathematical approaches to multi-criteria evaluation and many techniques for determining utility coefficients. The large discrepancy between the available methodologies leads to ambiguity in the assessments, so that the practical requirements for repeatability and uniqueness are often not met. The development of research on multi-criteria optimization, however, resulted in paying more attention to the multi-purpose and multi-aspect nature of solutions, as well as leading to the extension of the assessment of individual variants, which has a positive impact on the accuracy and rationality of the decisions made. One of the most commonly used methods of MCA is the weighted sum method (WSM). According to the WSM method, the following formulas were used in this study [44]:

$$a_{ij} = \frac{Indicator - Indicator_{min}}{Indicator_{max} - Indicator_{min}} \quad (1)$$

$$A_i = \sum\nolimits_{i-1}^{n} (a_{ij} \cdot w_j) \quad (2)$$

where a_{ij} is the normalized value of the *j*th indicator, A_i is the WSM score of alternative *I*, and w_j is the weighting factor for the *j*th indicator.

The overall score of each alternative is equal to the sum of the scores for all particular criteria, taking into account their weighting factors. Normalization of all alternatives to the same common scale in order to conduct a reasonable comparison is very important. In this study, the sum of normalized, equally weighted indicators was used for the final recommendation.

3. Results

In the following section, the results of the environmental, technical, and economic assessments of the modeled scenarios are presented. All of the particular calculations were then applied to identify the most environmentally friendly and cost-effective way of treating the lignocellulosic biomass in terms of obtaining the highest methane yields.

3.1. Results of Selected Criterion Analysis

The environmental analysis based on life cycle assessment allowed for the calculation of several impact indicators. First of all, the cumulative energy demand (CED) expressing the energy footprint of methane production processes, divided into unit processes, is presented in Figure 2.

	S1	S2	S3	S4	S5
harvesting, transporting	47.03	40.17	40.4	38.86	43.25
cutting 2-3cm	0.0004	0.0004	0.0004	0.0004	0.0004
smashing 0.38-0.83 mm	0.002	-	-	0.002	0.002
anaerobic digestion	152.11	129.91	130.67	125.69	139.88
grinding 0.25-0.38 mm	-	0.033	-	-	-
grinding <0.18mm	-	-	0.059	-	-
NaOH	-	-	-	37.82	42.09
steam bath 24h	-	-	-	15.39	-
ice cooling	-	-	-	0.94	1.04
HCl	-	-	-	54.74	60.92
autoclave 1h	-	-	-	-	2.25

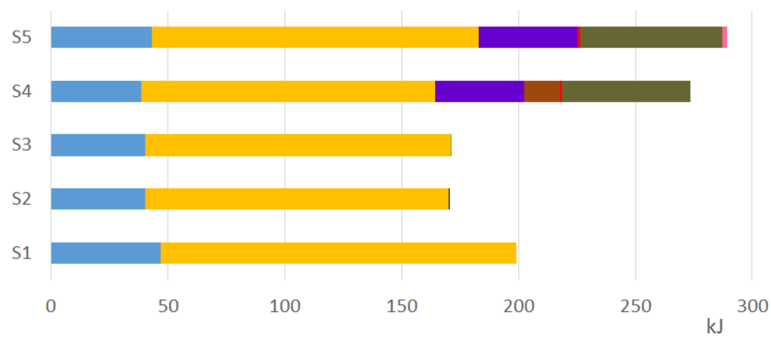

Figure 2. Cumulative Energy Demand per 1 dm^3 of Produced Methane in S1–S5 Processes.

Although the input material was harvested in the same way, the contribution of this unit process differed for various scenarios due to the selected functional unit (1 dm^3 of produced methane). In all the cases, the main contribution was connected with the anaerobic digestion process; for scenarios S4 and S5, the significant impact was related to the chemical substrates of the process. The Monte Carlo analysis in the case of this indicator allowed estimating the standard deviation of results not exceeding 0.01 MJ with a 95% confidence interval.

The global warming potential (Figure 3) was also calculated for the analyzed scenarios. The main contribution was connected with the anaerobic digestion process in all the cases as well as with the chemical substrates of the S4 and S5 processes. The Monte Carlo analysis in the case of this indicator allowed estimating the standard deviation of results not exceeding 0.0014 $kgCO_2eq$ with a 95% the confidence interval.

	S1	S2	S3	S4	S5
harvesting, transporting	0.0004	0.0003	0.0003	0.0003	0.0003
cutting 2-3 cm	$6x10^{-8}$	$5x10^{-8}$	$5x10^{-8}$	$5x10^{-8}$	$6x10^{-8}$
smashing 0.38-0.83 mm	$3x10^{-7}$	-	-	$2x10^{-7}$	$3x10^{-7}$
anaerobic digestion	0.0223	0.019	0.0192	0.0184	0.0205
grinding 0.25-0.38 mm	-	$5x10^{-6}$	-	-	-
grinding < 0.18	-	-	$9x10^{-6}$	-	-
NaOH	-	-	-	0.0025	0.0027
steam bath 24h	-	-	-	0.0023	-
ice cooling	-	-	-	$7x10^{-5}$	$8x10^{-5}$
HCl	-	-	-	0.0027	0.0031
autoclave 1h	-	-	-	-	0.0003

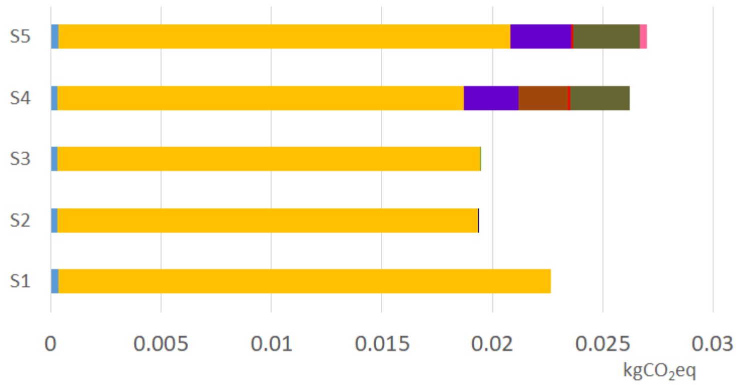

Figure 3. Global Warming Potential per 1 dm^3 of produced methane in the S1–S5 processes.

Furthermore, the IMPACT 2002+ indicator (Figure 4) was used to express the overall environmental effects related to selected processes of methane production. In the case of this particular indicator, the contribution of anaerobic digestion was even higher than in previous methods, which led to the conclusion that the energy consumption in this unit process was the most important issue. The fifth scenario (S5) was continuously responsible for the highest value of the indicator, while scenarios S2 and S3 present the lowest environmental impacts. The Monte Carlo analysis in the case of this indicator allowed estimating the standard deviation of results not exceeding 0.0012 mPt with a 95% confidence interval.

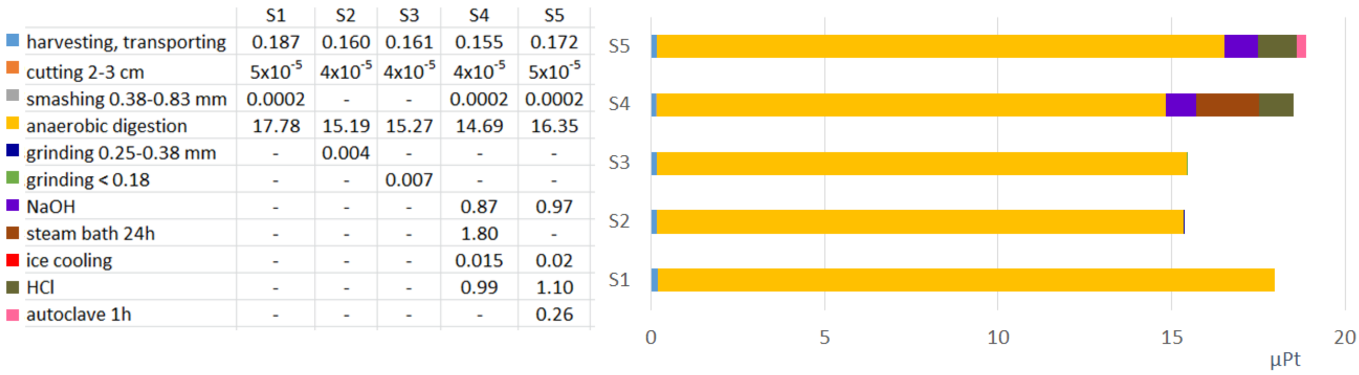

Figure 4. IMPACT 2002+ per 1 dm^3 of produced methane in the S1–S5 processes.

The cost of methane production per 1 dm^3 of released methane was also calculated. Obtained in particular scenarios (from S1 to S5), the values of cost were as follows: 1.83 EUR, 1.56 EUR, 1.57 EUR, 1.80 EUR, and 1.95 EUR, respectively.

The T_{80} values for each scenario were taken from the data presented by Kang et al. [9] and Kang et al. [47]. These values, in days, for S1 to S5 scenarios were 8, 11, 9, 4, and 3, respectively.

3.2. WSM Results

The indicators calculated in the above part of the study formed the basis of the normalization process (Table 1), which allowed selection of the preferred scenario. All parameters except T_{80} were converted to 1 dm^3 of methane produced in the anaerobic digestion process.

Table 1. Summary of the results obtained for the analyzed criteria.

Parameter	Unit	Scenarios				
		S1	**S2**	**S3**	**S4**	**S5**
IMPACT	µPt	17.97	15.35	15.44	18.52	18.87
CED	kJ	199.14	170.11	171.13	273.44	289.43
GWP100a	kg CO_2 eq	0.0227	0.0194	0.0195	0.0262	0.0270
T_{80} *	d	8	11	9	4	3
COST	EUR	1.83	1.56	1.57	1.80	1.95

* T_{80} values determined in literature [9,47].

According to the normalized WSM results presented in Figure 5, Scenario 3 (mechanical grinding of the substrate to a size of 0.18 mm) as well as Scenario 2 (mechanical grinding of the substrate to a size range of 0.25–0.38 mm) were the most beneficial. The only unpreferred criterion was T_{80} in these cases, while chemical preparation of samples (S4 and S5) resulted in a significant increase in environmental criterion indices.

It is also worth underlining that the higher cost of methane production in S4 and S5 was connected with both energy and chemical substrate consumption in the pretreatment processes. The cost of chemicals was 15% of the total methane production cost in these scenarios. Moreover, one needs to notice that the S4 and S5 scenarios were not reasonable since their WSM indicators were higher than those for the S1 scenario (without additional pretreatment).

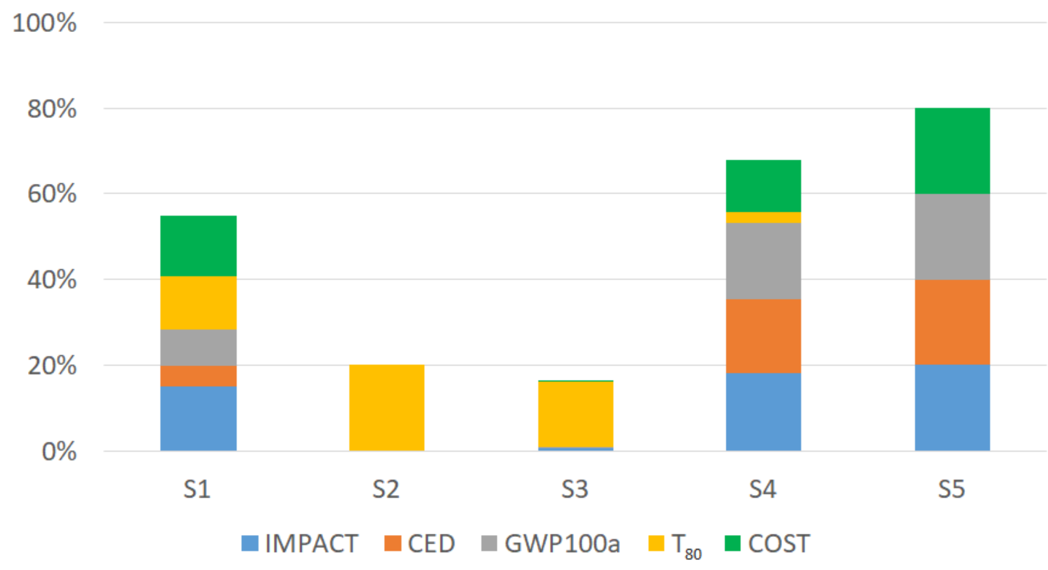

Figure 5. The normalized WSM indicator for the analyzed scenarios S1–S5.

4. Discussion

The paper presents a multi-criteria analysis of different scenarios of *Pennisetum hybrid* pretreatment before anaerobic digestion using the weighted sum method.

The results of this research show that the methods of mechanical grinding turned out to be the most advantageous in the analysis of the pretreatment process and the anaerobic digestion of lignocellulosic material. Taking into account the technical criteria, the main factor responsible for this result is the high production of methane with relatively low energy expenditure for the process. Mechanical pretreatment methods are believed to be simple and do not generate the compounds that could inhibit anaerobic digestion [57]. In general, the energy consumption of the mechanical pre-treatment process is a function of the type of biomass and moisture content [58] and also depends on the properties of the grinding device: machine variables and the feed rate of the material [59]. Therefore, some authors pointed to the fact that mechanical pretreatment methods are energy inefficient, i.e., the required energy inputs are not balanced by the energy generated in anaerobic digestion [58,60]. In the case of the analysis conducted for the S2 and S3 scenarios, the additional energy input into the process was balanced by additional methane yields (see BMP results).

In energy efficiency, the opposite results were obtained for chemical pretreatment methods in the S4 and S5 scenarios. In this case, the maximum improvement in methane yield was about 21%, which turns out to be insufficient to compensate for the costs incurred in the process. In this study, the highest cost per 1 dm^3 of produced methane was calculated for the S5 scenario with alkaline pretreatment (1.95 EUR). It exceeded the cost noted for the untreated sample by 0.12 EUR. Similarly, Zheng et al. [12] suggested that chemical pretreatment of biomass is not recommended because of economic reasons. Eggeman and Elander [61] as well as Hendriks and Zeeman [62] reached the same conclusions. Additionally, the difficulties with recycling NaOH or the treatment of process effluent contributed to the overall results of the comparison and were also an obstacle to commercialization and transfer under technical conditions [63]. At the same time, despite the high cost of the process, some researchers indicated very good results from the chemical pretreatment of lignocellulosic biomass. The methane yield of NaOH-pretreated corn straw increased by 73.4% compared to the value obtained for the untreated straw [59]. In general, the effectiveness of the alkaline pretreatment depends on the physical properties and chemical structure of the substrate, and it was stated that it was higher in the case of a biomass with lower lignin content than with substrates with high levels of lignin [63].

The pretreatment process, in addition to increasing methane production, can also accelerate the anaerobic digestion process as well as reduce the time needed for complete degradation of organic substances contained in the substrate [64]. The highest potential of time reduction in this study was observed in scenarios S4 and S5, where T_{80} was lower by 4 and 5 days, respectively, in comparison to the value obtained in scenario S1 (without grinding and alkaline pretreatment). This means that the technical digestion time decreased by 50 and 62.5%, respectively. The first value is in the range given by Delgenes et al. for the T_{80} reduction (23–59%) [65], while the second one is only slightly above that range. It seems that alkaline pretreatment of lignocellulosic biomass had a positive influence on substrate parameters in terms of decreasing the time needed to attain 80% of the methane volume at the anaerobic stage of the whole process. What is more, lower T_{80} was noted in scenario S4, in which a higher temperature of pretreatment was used. It may indicate a positive effect of pretreatment temperature on shortening the anaerobic digestion time [9]. The positive influence of alkaline pretreatment on lowering T_{80} was also observed by Di Girolamo et al. [66], who studied the influence of NaOH on three types of lignocellulosic substrates. The technical digestion time decreases obtained in their experiment were in the range from 9.4% to 48.4%. Similar results were noted by Sun et al. [67]. These authors observed the reduction of technical digestion time in the case of all previously pretreated samples subjected to anaerobic digestion in comparison to untreated ones (alkaline, alkaline hydrogen peroxide, electrochemically produced NaOH-H_2O_2, and electrohydrolysis pretreatment methods were used). The noted reduction degrees were in the range of 5.9 to 32.4%. When analyzing the values of T_{80} obtained in the scenarios S2 and S3 (with mechanical pretreatment), it can be stated that grinding the biomass to a smaller particle size (<0.18 mm) resulted in a reduction of this parameter in comparison to the value achieved in the variant with particles of 0.25–0.38 mm. The time was shortened from 11 to 9 days [47]. It was probably connected with increasing the available specific surface area resulting from finer grinding and being beneficial for the action of hydrolytic enzymes in microorganisms. Some authors stated that the T_{80} decrease observed after submitting the pretreated biomass to anaerobic digestion may be due to the reduction in degree of polymerization that is the result of pretreatment [62].

The results of the environmental analysis showed that mechanical pretreatment had lower environmental implications as compared to chemical pretreatment methods. Both in relation to the biomass not subjected to additional pretreatment and as compared to chemical methods, mechanical pretreatment performed better in terms of all analyzed environmental criteria (CED, GWP100a, and IMPACT). This situation is mainly caused by the fact that the S4 and S5 scenarios were burdened with high energy consumption by the thermostatic water bath and the autoclave, as well as by the consumption of chemical substrates. Similar results in the field of LCA analysis of lignocellulosic biomass pretreatment methods were obtained by Prasad et al. [41], where the chemical method using dilute acid performed the worst in nearly all of the analyzed impact categories. This was due to the long treatment and high energy inputs required to maintain a temperature of 60 °C at that time. Thus, the high energy consumption of pretreatment processes contributed the most to the increase in environmental indicators. It should be emphasized that the scenarios analyzed in the study are based on a laboratory balance of material and energy inputs; therefore, they may be burdened with an overestimation of these inputs due to the small scale of the base experiment. It is clearly visible in the case of CED results, where energy consumption determined the overall outcomes of comparisons between scenarios.

The results of the multi-criteria analysis depended on the functional unit, the adopted impact criteria, and the weights assigned to them. In this paper, the same weights were adopted for all the analyzed criteria in relation to the unit of 1 dm^3 of produced methane. It is worth noting that if the functional unit were the mass of the lignocellulosic biomass sample, the results of this analysis would be quite different. In that case, the environmental analysis indicators will be most favorable for the S1 scenario, which is not preferred due to the efficiency of methane production. Thus, this analysis allows looking at the pretreatment methods from a broader perspective, including the impact of different types of criteria, which can be helpful as influential instruments in technological and investment decision-making processes.

5. Conclusions

The results of the current study provide important insights on the optimization of the pretreatment and the anaerobic digestion of *Pennisetum hybrid* in terms of environmental impact as well as technical and energy indicators. The results of the multi-criteria analysis of the five scenarios, taking into account five criteria: CED, GWP100a, IMPACT, T_{80} and COST related to 1 dm^3 of methane production, indicated the significance of mechanical pretreatment methods. The most advantageous solution turned out to be the S3 scenario with grinding the biomass into a particle size range <0.18 mm.

It would be valuable to extend this research to a technical scale, which will simplify further deep analysis in the range of environmental impact categories and scenarios of fossil fuel substitution.

Author Contributions: Conceptualization, A.P. and M.B.; methodology, A.P.; software, M.Z., and A.P.; validation, M.Z. and M.B.; formal analysis, A.P.; investigation, M.B. and M.Z.; resources, A.P.; data curation, M.Z.; writing—original draft preparation, M.Z. and M.B.; writing—review and editing, A.P.; visualization, M.B.; supervision, M.B. and M.Z.; project administration, M.Z. and M.B.; funding acquisition, M.Z. and M.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Science and Higher Education as a part of subvention: grant numbers FD-20/IS-6/001 and FD-20/IS-6/040.

Data Availability Statement: Data and materials are available from the authors upon request.

Acknowledgments: We would like to thank Agnieszka Żelazna for support and technical assistance with the SimaPro software.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Shirzad, M.; Panahi, H.K.S.; Dashti, B.B.; Rajaeifar, M.A.; Aghbashlo, M.; Tabatabaei, M. A comprehensive review on electricity generation and GHG emission reduction potentials through anaerobic digestion of agricultural and livestock/slaughterhouse wastes in Iran. *Renew. Sust. Energy Rev.* **2019**, *111*, 571–594. [CrossRef]
2. Bilal, M.; Iqbal, H.M.N. Recent advancements in the Life Cycle Analysis of lignocellulosic biomass. *Curr. Sust. Renew. Energy Rep.* **2020**, *7*, 100–107.
3. Ziemiński, K.; Romanowska, I.; Kowalska-Wentel, M.; Cyran, M. Effects of hydrothermal pretreatment of sugar beet pulp for methane production. *Bioresour. Technol.* **2014**, *166*, 187–193. [CrossRef] [PubMed]
4. Aghbashlo, M.; Mandegari, M.; Tabatabaei, M.; Farzad, S.; Soufiyan, M.M.; Görgens, J.F. Exergy analysis of a lignocellulosic-based biorefinery annexed to a sugarcane mill for simultaneous lactic acid and electricity production. *Energy* **2018**, *149*, 623–638. [CrossRef]
5. Rebello, S.; Anoopkumar, A.N.; Aneesh, E.M.; Sindhu, R.; Binod, P.; Pandey, A. Sustainability and life cycle assessments of lignocellulosic and algal pretreatments. *Bioresour. Technol.* **2020**, *30*, 122678. [CrossRef]
6. Soltanian, S.; Aghbashlo, M.; Almasi, F.; Hosseinzadeh-Bandbafha, H.; Nizami, A.S.; Ok, Y.S.; Lam, S.S.; Tabatabaei, M. A critical review of the effects of pretreatment methods on the exergetic aspects of lignocellulosic biofuels. *Energy Convers. Manag.* **2020**, *212*, 112792. [CrossRef]
7. Mirmohamadsadeghi, S.; Karimi, K.; Azarbaijani, R.; Parsa Yeganeh, L.; Angelidaki, I.; Nizami, A.S.; Bhat, R.; Dashora, K.; Vijay, V.K.; Aghbashlo, M.; et al. Pretreatment of lignocelluloses for enhanced biogas production: A review on influencing mechanisms and the importance of microbial diversity. *Renew. Sust. Energy Rev.* **2021**, *135*, 110173. [CrossRef]
8. Muldoon, D.K. Simulation of *Hybrid Pennisetum* production in Australia. *Agric. Syst.* **1979**, *4*, 39–47. [CrossRef]
9. Kang, X.; Sun, Y.; Li, L.; Kong, X.; Yuan, Z. Improving methane production from anaerobic digestion of *Pennisetum Hybrid* by alkaline pretreatment. *Bioresour. Technol.* **2018**, *255*, 205–212. [CrossRef]
10. Moiser, N.; Wyman, C.; Dale, B.; Elander, R.; Lee, Y.Y.; Holtzapple, M.; Ladisch, M. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour. Technol.* **2005**, *96*, 673–686. [CrossRef]
11. Karki, B.; Maurer, D.; Jung, S. Efficiency of pretreatments for optimal enzymatic saccharification of soybean fiber. *Bioresour. Technol.* **2011**, *102*, 6522–6528. [CrossRef] [PubMed]

12. Zheng, Y.; Zhao, J.; Xu, F.; Li, Y. Pretreatment of lignocellulosic biomass for enhanced biogas production. *Prog. Energy Combust. Sci.* **2014**, *42*, 35–53. [CrossRef]
13. Alvira, P.; Tomás-Pejó, E.; Ballesteros, M.; Negro, M.J. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresour. Technol.* **2010**, *101*, 4851–4861. [CrossRef] [PubMed]
14. Harmsen, P.; Huijgen, W.; Bermudez, L.; Bakker, R. *Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass*; Wageningen UR Food & Biobased Research: Wageningen, The Netherlands, 2010.
15. Akhand, M.M.; Blancas, A.M. Optimization of NMMO Pretreatment of Straw for Enhanced Biogas Production. Master Thesis, University of Borås, Borås, Sweden, 2012.
16. Rodriguez, C.; Alaswad, A.; El-Hassan, Z.; Olabi, A.G. Improvement of methane production from *P. canaliculata* through mechanical pretreatment. *Renew. Energy* **2018**, *19*, 73–78. [CrossRef]
17. Muller, J.A.; Winter, A.; Struenkmann, G. Investigation and assessment of sludge pre-treatment processes. *Water Sci. Technol.* **2004**, *49*, 97–104. [CrossRef] [PubMed]
18. Mosier, N.; Hendrickson, R.; Ho, N.; Sedlak, M.; Ladisch, M.R. Optimization of pH controlled liquid hot water pretreatment of corn stover. *Bioresour. Technol.* **2005**, *96*, 1986–1993. [CrossRef] [PubMed]
19. Song, Z.; Yang, G.; Liu, X.; Yan, Z.; Yuan, Y.; Liao, Y. Comparison of seven chemical pretreatments of corn straw for improving methane yield by anaerobic digestion. *PLoS ONE* **2014**, *9*, e93801. [CrossRef]
20. Li, J.H.; Zhang, R.H.; Siddhu, M.A.H.; He, Y.F.; Wang, W.; Li, Y.Q.; Chen, C.; Liu, G.Q. Enhancing methane production of corn stover through a novel way: Sequent pretreatment of potassium hydroxide and steam explosion. *Bioresour. Technol.* **2015**, *181*, 345–350. [CrossRef]
21. Mathew, A.K.; Chaney, K.; Crook, M.; Humphries, A.C. Dilute acid pretreatment of oilseed rape straw for bioethanol production. *Renew. Energy* **2011**, *36*, 2424–2432. [CrossRef]
22. Behera, S.; Arora, R.; Nandhagopal, N.; Kumar, S. Importance of chemical pretreatment for bioconversion of lignocellulosic biomass. *Renew. Sust. Energy Rev.* **2014**, *36*, 91–106. [CrossRef]
23. Kumar, B.; Bhardwaj, N.; Agrawal, K.; Chaturvedi, V.; Verma, P. Current perspective on pretreatment technologies using lignocellulosic biomass: An emerging biorefinery concept. *Fuel Process. Technol.* **2020**, *199*, 106244. [CrossRef]
24. Naik, G.P.; Poonia, A.K.; Chaudhari, P.K. Pretreatment of lignocellulosic agricultural waste for delignification, rapid hydrolysis, and enhanced biogas production: A review. *J. Indian Chem. Soc.* **2021**, *98*, 100147. [CrossRef]
25. Durairaj, S.K.; Ong, S.K.; Nee, A.Y.C.; Tan, R.B.H. Evaluation of Life Cycle cost analysis methodologies. *Corp. Environ. Strategy* **2002**, *9*, 30–39. [CrossRef]
26. Borrion, A.L.; McManus, M.C.; Hammond, G.P. Environmental life cycle assessment of lignocellulosic conversion to ethanol: A review. *Renew. Sust. Energy Rev.* **2012**, *16*, 4638–4650. [CrossRef]
27. Torabi, F.; Ahmadi, P. Battery technologies. In *Simulation of Battery Systems*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 1–54.
28. Lewandowska, A. Environmental life cycle assessment as a tool for identification and assessment of environmental aspects in environmental management systems (EMS) part 1: Methodology. *Int. J. LCA* **2011**, *16*, 178–186. [CrossRef]
29. Cherubini, F.; Ulgiati, S. Crop residues as raw materials for biorefinery systems—A LCA case study. *Appl. Energy* **2010**, *87*, 47–57. [CrossRef]
30. Borrion, A.L.; McManus, M.; Hammond, G. Environmental life cycle assessment of bioethanol production from wheat straw. *Biomass Bioenergy* **2012**, *47*, 9–19. [CrossRef]
31. Turdera, M. Energy balance, forecasting of bioelectricity generation and greenhouse gas emission balance in the ethanol production at sugarcane mills in the state of Mato Grosso do Sul. *Renew. Sust. Energy Rev.* **2013**, *19*, 582–588. [CrossRef]
32. Liu, B.; Wang, F.; Zhang, B.; Bi, J. Energy balance and GHG emissions of cassava-based fuel ethanol using different planting modes in China. *Energy Policy* **2013**, *56*, 210–220. [CrossRef]
33. González-García, S.; Mola-Yudego, B.; Murphy, R.J. Life cycle assessment of potential energy uses for short rotation willow biomass in Sweden. *Int. J. LCA* **2013**, *18*, 783–795. [CrossRef]
34. Nuss, P.; Gardner, K.H. Attributional life cycle assessment (ALCA) of polyitaconic acid production from northeast US softwood biomass. *Int. J. LCA* **2013**, *18*, 603–612. [CrossRef]
35. Chen, L.; Pelton, R.E.; Smith, T.M. Comparative life cycle assessment of fossil and bio-based polyethylene terephthalate (PET) bottles. *J. Clean. Prod.* **2016**, *137*, 667–676. [CrossRef]
36. Aryapratama, R.; Janssen, M. Prospective life cycle assessment of bio-based adipic acid production from forest residues. *J. Clean. Prod.* **2017**, *164*, 434–443. [CrossRef]
37. Patel, M.K.; Bechu, A.; Villegas, J.D.; Bergez-Lacoste, M.; Yeung, K.; Murphy, R.; Woods, J.; Mwabonje, O.N.; Ni, Y.; Patel, A.D.; et al. Second-generation bio-based plastics are becoming a reality-non-renewable energy and greenhouse gas (GHG) balance of succinic acid-based plastic end products made from lignocellulosic biomass. *Biofuel. Bioprod. Biorefin.* **2018**, *12*, 426–441. [CrossRef]

38. Bello, S.; Salim, I.; Méndez-Trelles, P.; Rodil, E.; Feijoo, G.; Moreira Maria, T. Environmental sustainability assessment of HMF and FDCA production from lignocellulosic biomass through life cycle assessment (LCA). *Holzforschung* **2018**, *73*, 105–115. [CrossRef]
39. Chuetor, S.; Champreda, V.; Laosiripojana, N. Evaluation of combined semi-humid chemo-mechanical pretreatment of lignocellulosic biomass in energy efficiency and waste generation. *Bioresour. Technol.* **2019**, *292*, 121966. [CrossRef]
40. Kumar, D.; Murthy, G.S. Life cycle assessment of energy and GHG emissions during ethanol production from grass straws using various pretreatment processes. *Int. J. LCA* **2012**, *17*, 388–401. [CrossRef]
41. Prasad, A.; Sotenko, M.; Blenkinsopp, T.; Coles, S.R. Life cycle assessment of lignocellulosic biomass pretreatment methods in biofuel production. *Int. J. LCA* **2016**, *21*, 44–50. [CrossRef]
42. Smullen, E.; Finnan, J.; Dowling, D.; Mulcahy, P. The environmental performance of pretreatment technologies for the bioconversion of lignocellulosic biomass to ethanol. *Renew. Energy* **2019**, *142*, 527–534. [CrossRef]
43. Van Fan, Y.; Klemeš, J.J.; Perry, S.; Lee, C.T. Anaerobic digestion of lignocellulosic waste: Environmental impact and economic assessment. *J. Environ. Manag.* **2019**, *231*, 352–363. [CrossRef]
44. Żelazna, A.; Gołębiowska, J.; Zdyb, A.; Pawłowski, A. A Hybrid vs. on-grid photovoltaic system: Multicriteria analysis of environmental, economic, and technical aspects in life cycle perspective. *Energies* **2020**, *13*, 3978. [CrossRef]
45. Müller-Langer, F.; Kaltschmitt, M. Biofuels from lignocellulosic biomass—A multi-criteria approach for comparing overall concepts. *Biomass Convers. Biorefin.* **2015**, *5*, 43–61. [CrossRef]
46. Vamza, I.; Valters, K.; Blumberga, D. Multi-criteria analysis of lignocellulose substrate pre-treatment, environmental and climate technologies. *Environ. Clim. Technol.* **2020**, *24*, 483–492. [CrossRef]
47. Kang, X.; Zhang, Y.; Song, B.; Sun, Y.; Li, L.; He, Y.; Kong, X.; Luo, X.; Yuan, Z. The effect of mechanical pretreatment on the anaerobic digestion of *Hybrid Pennisetum*. *Fuel* **2019**, *252*, 469–474. [CrossRef]
48. Huijbregts, M.A.; Hellweg, S.; Frischknecht, R.; Hendriks, H.W.; Hungerbühler, K.; Hendriks, A.J. Cumulative energy demand as predictor for the environmental burden of commodity production. *Environ. Sci Technol.* **2010**, *44*, 2189–2196. [CrossRef]
49. Arvesen, A.; Hertwich, E.G. More caution is needed when using life cycle assessment to determine energy return on investment (EROI). *Energy Policy* **2015**, *76*, 1–6. [CrossRef]
50. Hischier, R.; Weidema, B.; Althaus, H.J.; Bauer, C.; Doka, G.; Dones, R.; Nemecek, T. *Implementation of Life Cycle Impact Assessment Methods*; Swiss Centre for Life Cycle Inventories: Dübendorf, Switzerland, 2010.
51. Frischknecht, R.; Wyss, F.; Büsser Knöpfel, S.; Lützkendorf, T.; Balouktsi, M. Cumulative energy demand in LCA: The energy harvested approach. *Int. J. LCA* **2015**, *20*, 957–969. [CrossRef]
52. US EPA. Available online: https://www.epa.gov (accessed on 10 November 2022).
53. Cel, W.; Pawłowski, A.; Cholewa, T. Carbon footprint as a measure of sustainability of renewable energy sources. In *Diagnosing the State of the Environment. Research Methods—Forecasts*; Garbacz, J.K., Ed.; Prace Komisji Ekologii i Ochrony Środowiska, Bydgoskie Towarzystwo Naukowe: Bydgoszcz, Poland, 2010; pp. 15–22.
54. Jolliet, O.; Margni, M.; Charles, R.; Humbert, S.; Payet, J.; Rebitzer, G.; Rosenbaum, R. IMPACT 2002+: A new life cycle impact assessment methodology. *Int. J. LCA* **2003**, *8*, 324–330. [CrossRef]
55. Lelek, L.; Kulczycka, J.; Lewandowska, A.; Zarebska, J. Life cycle assessment of energy generation in Poland. *Int. J. LCA* **2016**, *21*, 1–14. [CrossRef]
56. European Biogas Association. Available online: https://www.europeanbiogas.eu/ (accessed on 24 October 2022).
57. Khan, M.U.; Usman, M.; Ashraf, M.A.; Dutta, N.; Luo, G.; Zhang, S. A review of recent advancements in pretreatment techniques of lignocellulosic materials for biogas production: Opportunities and limitations. *Chem. Eng. J. Adv.* **2022**, *10*, 100263. [CrossRef]
58. de Oliveira, M.C.; Bassin, I.D.; Cammarota, M.C. Microalgae and cyanobacteria biomass pretreatment methods: A comparative analysis of chemical and thermochemical pretreatment methods aimed at methane production. *Fermentation* **2022**, *8*, 497. [CrossRef]
59. Amin, F.R.; Khalid, H.; Zhang, H.; Rahman, S.U.; Zhang, R.; Liu, G.; Chen, C. Pretreatment methods of lignocellulosic biomass for anaerobic digestion. *AMB Express* **2017**, *7*, 72. [CrossRef]
60. Córdova, O.; Passos, F.; Chamy, R. Physical pretreatment methods for improving microalgae anaerobic biodegradability. *Appl. Biochem. Biotechnol.* **2018**, *185*, 114–126. [CrossRef] [PubMed]
61. Eggeman, T.; Elander, R.T. Process and economic analysis of pretreatment technologies. *Bioresour. Technol.* **2005**, *96*, 2019–2025. [CrossRef] [PubMed]
62. Hendriks, A.T.W.M.; Zeeman, G. Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresour. Technol.* **2009**, *100*, 10–18. [CrossRef]
63. Chen, Y.; Stevens, M.A.; Zhu, Y.; Holmes, J.; Xu, H. Understanding of alkaline pretreatment parameters for corn stover enzymatic saccharification. *Biotechnol. Biofuels* **2013**, *6*, 8. [CrossRef] [PubMed]
64. Meegoda, J.N.; Li, B.; Patel, K.; Wang, L.B. A review of the processes, parameters, and optimization of anaerobic digestion. *Int. J. Environ. Res. Public Health* **2018**, *15*, 2224. [CrossRef]
65. Delgenes, J.P.; Penaud, V.; Moletta, R. Pretreatments for the Enhancement of Anaerobic Digestion of Solid Wastes. In *Biomethanization of the Organic Fraction of Municipal Solid Waste*; Mata-Alvarez, J., Ed.; 13 IWA Publishing: London, UK, 2003; pp. 201–228.

66. Di Girolamo, G.; Bertin, L.; Capecchi, L.; Ciavatta, C.; Barbanti, L. Mild alkaline pre-treatments loosen fibre structure enhancing methane production from biomass crops and residues. *Biomass Bioenergy* **2014**, *71*, 318–329. [CrossRef]
67. Sun, S.; Zhang, Y.; Yang, Z.; Liu, C.; Zuo, X.; Tang, Y.; Wan, P.; Liu, Y.; Li, X.; Coulon, F.; et al. Improving the biodegradability of rice straw by electrochemical pretreatment. *Fuel* **2022**, *330*, 125701. [CrossRef]