# From Cardoon Lignocellulosic Biomass to Bio-1,4 Butanediol: An Integrated Biorefinery Model

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Keywords: BDO, bioeconomy, integrated biorefinery, 2G sugars, lignocellulosic biomass

#### Abstract:

Biorefineries are novel, productive models that are aimed at producing biobased alternatives to many fossil-based products. Biomass supply and overall energy consumptions are important issues determining the overall biorefinery sustainability. Low-profit lands appear to be a potential option for the sustainable production of raw materials without competition with the food chain. Cardoon particularly matches these characteristics, thanks to the rapid growth and the economy of the cultivation and harvesting steps. An integrated biorefinery processing 60 kton/y cardoon lignocellulosic biomass for the production of 1,4-butanediol (bio-BDO) is presented and discussed in this work. After designing the biorefinery flowsheet, the mass and energy balances were calculated. The results indicated that the energy recovery system has been designed to almost completely cover the entire energy requirement of the BDO production process. Despite the lower supply of electricity, the energy recovery system can cover around 78% of the total electricity demand. Instead, the thermal energy recovery system was able to satisfy the overall demand of the sugar production process entirely, while BDO purification columns require high-pressure steam. The thermal energy recovery system can cover around 83% of the total thermal demand. Finally, a cradle-to-gate simplified environmental assessment was conducted in order to evaluate the environmental impact of the process in terms of carbon footprint. The carbon footprint value calculated for the entire production process of BDO was 2.82 kgCO2eq/kgBDO. The cultivation phase accounted for 1.94 kgCO2eq/kgBDO, the transport had very little impact, only for 0.067 kgCO2eq/kgBDO, while the biorefinery phase contributes for 0.813 kgCO2eq/kgBDO.

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Article

### From Cardoon Lignocellulosic Biomass to Bio-1,4 Butanediol: An Integrated Biorefinery Model

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Abstract: Biorefineries are novel, productive models that are aimed at producing biobased alternatives to many fossil-based products. Biomass supply and overall energy consumptions are important issues determining the overall biorefinery sustainability. Low-profit lands appear to be a potential option for the sustainable production of raw materials without competition with the food chain. Cardoon particularly matches these characteristics, thanks to the rapid growth and the economy of the cultivation and harvesting steps. An integrated biorefinery processing 60 kton/y cardoon lignocellulosic biomass for the production of 1,4-butanediol (bio-BDO) is presented and discussed in this work. After designing the biorefinery flowsheet, the mass and energy balances were calculated. The results indicated that the energy recovery system has been designed to almost completely cover the entire energy requirement of the BDO production process. Despite the lower supply of electricity, the energy recovery system can cover around 78% of the total electricity demand. Instead, the thermal energy recovery system was able to satisfy the overall demand of the sugar production process entirely, while BDO purification columns require high-pressure steam. The thermal energy recovery system can cover around 83% of the total thermal demand. Finally, a cradle-to-gate simplified environmental assessment was conducted in order to evaluate the environmental impact of the process in terms of carbon footprint. The carbon footprint value calculated for the entire production process of BDO was 2.82 kg<sub>CO2ea</sub>/kg<sub>BDO</sub>. The cultivation phase accounted for 1.94 kg<sub>CO2ea</sub>/kg<sub>BDO</sub>, the transport had very little impact, only for 0.067 kg<sub>CO2eq</sub>/kg<sub>BDO</sub>, while the biorefinery phase contributes for 0.813 kg<sub>CO2eq</sub>/kg<sub>BDO</sub>.

Keywords: lignocellulosic biomass; 2G sugars; integrated biorefinery; bioeconomy; BDO

#### 1. Introduction

The increasing attention to environmental issues and the need to reduce fossil resources have led to creating new sustainable economic growth [1]. These models are based on the alternative and efficient use of raw materials waste or renewable in order to produce added value chemical intermediates or entirely bio-based products [2]. These products have a lower environmental impact than their fossil counterparts [3]. Their introduction on the market represents an excellent opportunity to develop local economic sectors, thanks to creating integrated, interconnected, and interdisciplinary local supply chains [4,5]. The utilization of marginal lands, not in competition with food production, for the



generation of renewable raw materials represents a tool for territorial regeneration with potentially positive effects on several fronts [4].

Among renewable sources, biomass represents the most sophisticated form of solar energy storage: through the photosynthesis process, plants can convert radiant energy into chemical energy and store it in the form of complex molecules high energy content [6]. For this reason, biomass is considered to be a renewable and inexhaustible resource if adequately used, or if the use rate does not exceed the regeneration capacity of the plant growing [7]. Lignocellulosic biomass can be converted to energy and chemicals by thermochemical (e.g., gasification [8]) or biological processes (e.g., sugars fermentation [9]).

Biomass is also considered to be a neutral energy source for increasing greenhouse gas emissions [10]. During the growth process, the plants contribute to the subtraction of atmospheric carbon dioxide and carbon fixation through photosynthesis [11].

Biomass-derived sugars are an important platform for many applications. Among these, 1,4-butanediol (1,4-BDO) is a large volume chemical with a global market approaching two million tons per year and it is used in many applications, which range from automotive plastics and electronics. 1,4-BDO is currently produced from fossil feedstocks (coal, oil, or natural gas) by four major energy-intensive processes and it is responsible for significant greenhouse gas emissions [12]. Growing concerns over the environment and volatile fossil energy costs inspired developing a more sustainable process for BDO production from renewable feedstocks with lower cost, lower energy consumption, and lower greenhouse gas emissions.

Applications of 1,4-BDO include:

- (a) Thanks to biodegradability, BDO has potent agriculture applications as a growth-promoting and pest control agent [13].
- (b) It is an organic solvent for industrial cleaners [14].
- (c) It represents a key chemical building block that is used to make polybutylene terephthalate (PBT), spandex (lycra, elastane), and polyurethanes [12].

Thus, the techno-economic/environmental assessment of BDO production has been widely studied in recent years.

Forte et al. [12] used the Life Cycle Assessment (LCA) approach to investigate the environmental performance of bio-based 1,4-butanediol (BDO) that is produced via direct fermentation of sugars from a wheat straw as part of a model regional biorefinery. Authors identified the hotspots along the production chain, and they assessed the potential environmental benefits of this bio-based polymer versus the conventional reference product (fossil-based BDO). The prevailing contribution to the total environmental impact of bio-based BDO was identified in the feedstock production and heat requirement at the biorefinery plant. On the contrary, the feedstock cultivation displayed lower impacts in terms of acidification and eutrophication.

Teh et al. [15] studied the fuzzy optimization approach that was applied to the economic performance, health, safety, and environmental impact of 1,4-butanediol production process. The developed input-output models were then optimized while using fuzzy optimization. The results from the case study indicated that the Davy process is more sustainable when compared to the Reppe process. The results suggested that the Davy process's operating capacity should be scaled down by 3.3% in order to meet the trade-of scores determined by the value obtained.

Satam et al. [16] studied the bio-based production route to 1,4-BDO to individuate the major capital and operating costs that are associated with production. Bioconversion was found to be the major capital cost component, while the hydraulic load from bioconversion and other systems, like membrane filtration, was found to be the major operating cost component. The process was economically feasible with a minimum sales price (MSP) of 1,4-BDO of \$1.82/kg as compared to a market price of \$2.5/kg.

A novel plant was recently inaugurated in northern Italy by a Novamont joint venture, Mater-biotech, in order to produce 1,4 BDO from sugars [16]. Novamont has developed, in Italy, a cardoon based biorefinery concept. In this value chain, lignocellulosic residues represent an abundant

raw material that can be locally available to produce biochemicals. Cardoon is a perennial herbaceous species native to the Mediterranean basin [17]. It can be cultivated for various uses, but it is mainly cultivated for energy purposes [18]. Epigean and hypogean lignocellulosic biomass are a valuable source for the multi-products lignocellulosic chain, while the achenes (seeds) are typically sent to the agri-food chain and the energy chain (biodiesel chain) [19]. The interest in cardoon as an multipurpose crop arises from the fact that it can be quickly grown in marginal or uncultivated land with low, if not wholly zero, water supplies (absence of irrigation) and limited use of herbicides [20]. Besides, when compared to other industrial crops for energy purposes, it has lower nutritional needs, provides for the annual collection of biomass, and does not require many soil tillage, with many benefits in terms of erosive risk and containment of carbon dioxide (CO<sub>2</sub>) emissions in the atmosphere [20]. Therefore, cardoon is a multipurpose crop that can be used as a raw material in order to produce many added value chemical intermediates and bioproducts of considerable industrial interest [19]. The oil that was extracted from the achenes can be usefully used in numerous sectors [21]. The oil extracted from thistle can also be transformed into biopolymers through a series of chemical passages yielding, for instance, azelaic acid and pelargonic acid [22]. The extraction flours (highly protein flours) can be

The lignocellulosic fraction represents a huge part of the plant and an integrated exploitation is advised to enhance the biorefinery sustainability. In this context, it is necessary to develop an integrated high energy efficiency supply and production chains

destined to the feed industry in partial or total replacement of genetically modified soybean meal or

used to produce active molecules that are to be used in the field of nutraceuticals [23].

With this finality, the present work describes the exploitation of the lignocellulosic residue for the production of second-generation sugars (2GS) and their subsequent conversion to 1,4-bio-Butanediol (bio-BDO). An integrated process flowsheet has been developed along with the corresponding sizing of the plants. A treatment capacity of 60 kton/year lignocellulosic residues has been assumed, which is compatible with local supply basins' typical potential. Finally, the material and energy balances were built accordingly, and a simplified analysis of the environmental impact was conducted by assessing the carbon footprint while using a LCA (Life Cycle Assessment) approach. The final scope of the paper is to quantitatively assess a novel biorefinery layout with the potential of being integrated in an existing oil-based value chain from cardoon.

#### 2. Materials and Methods

#### 2.1. The New Integrated Biorefinery Model

This section describes the process flowsheet for producing second-generation sugars (2GS) and the subsequent conversion to bio-BDO while using residual lignocellulosic thistle biomass as raw material.

Process data were, in part, gathered from literature and, in part, from process simulation and scaling using ENEA's facilities [24]. Data regarding the sugars concentration unit, the purification step following the in situ enzyme production, and the energy recovery sections derived from some technology providers' technical sheets, referred to the process scale, are considered in the present paper. Raw data were made homogenous through scaling factors and used to define material and energy balances [25] to obtain 2GS, first, and then bio-BDO. The cogeneration and wastewater treatment modules' main specifications were also included to evaluate the overall energy performance. The reference plant size was 60,000 t/year lignocellulosic biomass. The system's flow rate was 7485 kg/h while assuming a continuous process with an up-time of 334 working days per year (8016 h).

The entire plant was considered to be operating continuously, except for cases in which the equipment's operation is necessarily discontinuous (filtration) or fed-batch (enzyme production). Furthermore, all of the biological reactors present in the process layout were considered to be perfectly mixed, so the output concentrations were equal to the uniform ones within the same reactors. Besides, the biological conversion speeds were considered as constant and independent of the substrate concentrations. Figure 1 displays the overall process block diagram.



Figure 1. Process flowsheet for the bio-based 1,4-butanediol production from cardoon.

#### 2.2. Feedstock

The achenes (the main product of cardoon cultivation) are used for the production of oil. The stems and flower heads are lignocellulosic biomass that can be valorized through the intermediate production of sugars. Table 1 shows the composition of the residues and compares them with other lignocellulosic feedstocks. Because of the similar composition, the listed feedstock is likely to be converted through a similar process layout or even used in a multi feedstock feeding to face any need due to the raw seasonality material.

	Cellulose	Hemicellulose	Lignin
Cardoon	35%	18.9%	29.4%
Herbaceous	40%	22%	5-20%
Wheat straw	47-48%	19%	33-34%
Oats	40%	22%	38%
Corn stover	44%	26%	15-20%

Table 1. Mean composition of main residual cereal material [26].

#### 2.3. Second-Generation Sugars Production from Cardoon Residual Biomass

#### 2.3.1. Pretreatment via Steam Explosion

The biomass was fed to a steam explosion pretreatment plant and put under steam pressure (14 barg; 200 °C) for about 5–7 min. [27]. Immediately after that, it was instantly released to ambient conditions, so that its lignocellulosic structure was destructured and more easily fractionated into its three main components: cellulose, hemicellulose, and lignin. The input steam/dry biomass ratio was 1:1, while water and sulfuric acid  $H_2SO_4$  (12 g per kg of dry biomass) were added in order to facilitate the degradation process of the biomass [28].

#### 2.3.2. Hemicellulose Extraction

Hemicellulose is a water-soluble polysaccahride. The several process layouts weres, in principle, applicable. After the pretreatment step, cellulose and hemicellulose could be hydrolyzed in the same bioreactor. However, separate processes for the two streams were considered in this model for more flexible use of the C5 sugars. Unlike C6 sugars, microbial process converting C5 sugars often achieve low yields, which often implies the need for a dedicated optimization. In the present work, the use of H<sub>2</sub>SO<sub>4</sub> as an acid catalyst during the pretreatment favored almost complete hemicellulose hydrolysis [29]. This implied that hemicellulose did not need a dedicated step of enzymatic hydrolysis. On the other side, the mixed cellulose and hemicellulose hydrolysis would have the following disadvantages: residual xylan and soluble biomass degradation by-products could inhibit cellulases activities. The exploded product was fed into an extraction tank that was working at a solid-to-liquid ration S/L ratio = 0.15 while using a scheme in which part was recycled in order to extract fresh pulp, thus increasing the sugar concentration. The separated residues containing cellulose and lignin fibers were washed and filtered at the extractor outlet. The extraction temperature was 65 °C and the residence time of the hemicellulose inside the tank was about 30 min. [27].

#### 2.3.3. In Situ Enzyme Production

In this study, the in situ production of enzymes for the cellulose hydrolysis into glucose was considered. *Trichoderma Reesei* was selected as a model fungus for the secretion of enzymes. Part of the pretreated slurry was used as a substrate for growth. The following assumptions were made: enzymes produce 0.33 g/gC on the carbon substrate (C5 + C6) [30]. The process has been optimized in order to produce a final dosage of 19 FPU/gC6 for the cellulose hydrolysis phase [31].

#### 2.3.4. Enzyme Separation

The enzyme broth was clarified by the DIA microfiltration process to separate the inorganics, organic substances, and cell mass from the enzymes and substances that were dissolved in the aqueous solution [32].

#### 2.3.5. Hydrolysis of Cellulose

The clarified enzyme broth was added to the cellulose-rich stream for glucose production by the enzymatic hydrolysis process. This process was carried out through two different steps: liquefaction, with high stirring and relatively short residence time (200 rpm; 5 h;  $T = 50 \degree C$ ) and the completion of the saccharification, with less stirring and longer residence times (100 rpm; 48 h;  $T = 45 \degree C$ ) [33]. The solid/liquid ratio of the initial flow was 0.16, with a final hydrolysis yield of 80% [31].

#### 2.3.6. Compressed Air Filtration

After the hydrolysis of the cellulose, the glucose stream was subjected to a high-performance pressure filtration phase, by which the solid residues (containing lignin, organic wastes, and residual enzymes from the DIA filtration, inorganic) were separated with the minimum content humidity (40% by weight, in this case) in order to reduce the glucose losses and obtain an organic material with suitable characteristics as a solid fuel [34]. In particular, this process is useful to separate the lignin-rich stream to be sent to the cogeneration section for the lignin thermal valorization [35]. The air pressure filtration phase-separated the glucose from the unconverted cellulose and the exhausted cellulase proteins that were incorporated in the fibers.

#### 2.3.7. Sugar Concentration

The hemicellulose streams (xylan and xylose) and glucose were finally mixed in order to obtain a single sugar solution with a total concentration equal to approximately 90 g/L. Sugars were concentrated to molasses containing 600 g/L [36]. This contains microbial contaminations, and it could provide

concentrated feeds for continuous fermentation with a fed-batch feeding. Sugars had been concentrated through a falling film evaporator with five concentration levels. The initial vapor pressure of 10-bar and the final phase at 0.125-bar had been hypothesized. This system solution allowed for obtaining a product stream with a final concentration of 600 g/L and removing most of the microbial inhibitors due to evaporation and stripping [37].

#### 2.3.8. Wastewater Treatment

The liquid wastes though the overall sugars production comprise the condensed steam that is released during the pretreatment via Steam Explosion and the condensed fractions through the falling film evaporators and the BDO purification step. Both of these streams contain dissolved organic compounds (i.e., furfural, 5HMF, short-chain organic acids), which could be converted into biogas (35% CH<sub>4</sub> and 65% CO<sub>2</sub> by weight) through anaerobic digestion [38]. Therefore, the wastewater treatment section was conceived as consisting of a first anaerobic treatment phase, through which 90% of COD (14.6 g/L) was converted into biogas (0.229 gCH<sub>4</sub>/gCOD) [30], and from a second biological aerobic phase, through which 90% of residual COD was still removed (with the release of CO<sub>2</sub>). Finally, the wastewater was conveyed to a sedimentation basin, where the sludge was buried on the bottom, while the clean water was recovered from above. This water flow was then recycled for internal uses of the general process, while the mud was filtered and sent to the inert.

#### 2.3.9. Energy Recovery System

Residual streams of biogas, lignin (hydrolysis cake), and organic waste from enzymes production section were sent to the cogeneration section in order to recovery electrical/thermal energy. For the energy analysis, the installed power for each electrical and/or mechanical and its usage coefficient during the entire production process were estimated. The demand for thermal energy was also calculated for all phases of the process in terms of saturated process steam at 14-barg (for the Steam Explosion), steam at 10-barg of pressure (for the concentration of the sugar solution), and production of hot water at 70 °C for the rest of the thermal operation [39]. Therefore, the power and thermal energy balances were carried out by analyzing the net capacity (net of self-consumption) of a properly designed energy recovery system. Finally, an overall estimate of freshwater consumption was also made, while taking the possibility of recycling clean water from the wastewater treatment section into account. The energy recovery system aimed to produce energy, steam, and hot water (70 °C) for internal uses [30]. It mainly consisted of two lines: a cogeneration plant based on an internal combustion engine with biogas and a solid fuel combustion plant coupled to a steam boiler and turbine. In the first line, biogas from wastewater treatment was used and energy and hot water were produced. The second line was fed with organic solid residues from the air pressure filtration phase (hydrolysis cake), 40% humidity, about 9% of dry ash, and calorific value of less than 16,000 kJ/kg of weight. The retentate deriving from the enzymes purification process was also used for energy recovery. A combustion reactor (fluidized bed combustor) has been suitably designed for this special organic material (thermal efficiency of up to 95%). Superheated steam was produced at 480 °C and 65-barg, and the back pressure turbine was used for the production of energy in order to obtain 14-barg of downstream steam [40], to be used for the pretreatment of the explosion of steam. Subsequently, residual steam was used to concentrate the sugar solution and finally hot water (70 °C) was produced.

#### 2.4. Sugars Fermentation to BDO

With a final concentration of 600 g/L, the sugars-rich stream was sent to the BDO fermentation section. Process simulation and design methods [41] were used to assess the BDO fermentation and purification sections' material and energy balances.

#### 2.4.1. BDO Fermentation

The BDO fermentation was carried out in two stages, both being operated under aerobic conditions. The first stage occurred in a seed reactor, separate from the main bioreactor, in order to increase cell concentration of the engineered *E. coli* strain [14]. Both of the bioreactors were operated in a fed-batch mode to avoid too high glucose concentration values. After 30 h, the seed broth was transferred to the main bioconversion reactor, which contained the same composition as the initial seed medium. In order to minimize the impurities, after 37 h, the main bioreactor was considered to have stopped [16]. During the fed-batch process, the 600 g/L solution was added to bioreactors in order to have a constant concentration in the broth.

The theoretical yield from glucose was equal to 0.49  $g_{BDO}/g_{GLUCOSE}$ . The fermentation yield to BDO was fixed to 0.46  $g_{BDO}/g_{GLUCOSE}$ . Xylose contribution to the total yield was assumed to be equal to 0.04  $g_{BDO}/g_{XYLOSE}$  [42].

The main reactions considered was:

$$C_6H_{12}O_6 \rightarrow C_4H_{10}O_2 + 2CO_2 + H_2$$
  
 $C_5H_{10}O_5 + H_2 \rightarrow C_4H_{10}O_2 + CO_2 + H_2O_2$ 

#### 2.4.2. BDO Purification

Figure 2 shows the process flowsheet that is used to simulate the BDO fermentation and purification sections. Membrane technologies were considered to separate microorganisms and unconverted sugars from the broth [43].



Figure 2. Process simulation flowsheet for the BDO fermentation and purification.

The heater was used to reach the boiling point of the mixture.

The recovery of BDO was done by distillation. Water has a higher relative volatility than BDO, since the boiling point of BDO was more than 180 °C, and it does not form an azeotrope with water. This means that it was easily separated from water while using conventional distillation. Partial condenser was used to have two phases from the top of the column. The water was completely removed from the distillate along with  $CO_2$ , while the remaining BDO was taken from the bottom stream [44].

#### 2.5. Environmental Impact Analysis

The methodology used for the analysis of the environmental impact and the calculation of the carbon footprint is reported in the European Directive 2009/28/EC "Renewable Energy Directive" (RED). Always being linked to a life cycle approach, it was created to quantify GHG gas emissions from biofuels and bioliquids' production and use. The methodology does not take the  $CO_2$  captured during the biomass growth phase into account. At the same time, the emissions that were related to the use phase of the biofuel were considered to be zero.

The  $CO_{2eq}$  emission values used to obtain the impact values in terms of  $CO_2$  equivalent, multiplying the input values of the entire production process by the appropriate coefficients that were obtained from LCA studies, carried out by a consortium led by the Joint Research Center, for the purpose of obtaining reference values (standard values) for GHG emissions related to the production of some biofuels. These standard values have been disclosed thanks to the European BioGrace project, whose aim was to harmonize GHG emissions calculations that must be carried out in compliance with the RED and Fuel Quality (FQD) directives [45,46].

Furthermore, in compliance with the RED methodology, the emissions that were related to the biogenic  $CO_2$  emitted during the process phases (combustion of biogas and lignin and aerobic digestion of condensates) were considered as equal to zero, being compensated by the  $CO_2$  sequestered during the biomass, whose credit was not taken into account.

For each process case, a final environmental impact analysis was performed in terms of total CO<sub>2</sub>-equivalent emission [35,47] by adopting the values that were reported in the work of Alberici and Hamelinck [48]. In particular, this part of the work's goal was to evaluate the environmental impact of the production of BDO in a cardoon-based biorefinery in terms of carbon footprint. The production process of the BDO was divided into three phases, each being characterized by flows of materials and energy input (input) and flows of materials and energy output (output). The phases considered were:

- 1. the cultivation phase which includes the cultivation and harvesting of residual thistle biomass in the field;
- 2. transportation that involves the transportation of biomass that were collected from the field to the biorefinery plant;
- 3. the biorefinery phase or the transformation phase of the lignocellulosic residue into BDO.

The cultivation phase and the biorefinery phase represent the most complex phases. Unlike the transport phase, characterized by a single input, a single output, and a single operation (the transport itself), the other steps are characterized by a higher number of input and output data and by more operations. In the cultivation phase, the direct emissions of N<sub>2</sub>O that are linked to nitrogen fertilizers' application were calculated, as required by the RED methodology. In contrast, in the biorefinery phase, the emissions that were related to the wastewater treatment processes were taken into account, with the latter suitable for disposal. For the cultivation phase, the operations were the common agricultural operations: plowing the field, sowing, fertilization, irrigation (if provided), collection, and windrowing of biomass. For the biorefinery phase, the operations were those identified in the optimized process layout: biomass pretreatment, hemicellulose extraction, cellulose hydrolysis, filtration, concentration, enzyme production in situ, micro/ultrafiltration, effluent treatment, and energy recovery. The emissions that were related to the production of NaOH, AD13, CaOH<sub>2</sub>, and urea used in the effluent treatment processes were not considered due to the low flows involved and lack of available data.

The greenhouse gas emissions that were associated with the cultivation phase for 1 kg of residual biomass produced were equal to 0.23 kg<sub>CO2eq</sub>, where this value takes into account the allocation factor (AF = 0.66) calculated based on the economic value of the seeds and lignocellulosic residue, the raw material of the considered process.

The greenhouse gas emissions that were associated with the transport of 1 kg of biomass were instead equal to 0.0082  $kg_{CO2eq}$  in the hypothesis of traveling, from the field to the biorefinery for a maximum theoretical distance of 100 km (return) and transporting the residual biomass with a truck with a maximum load of 40 t (27 t loaded). The data come from previous agronomic research activities that were conducted by ENEA on experimental thistle fields regarding the cultivation phase. The starting point of these activities was an agricultural land left uncultivated for years. Table 2 shows the details of the experimental site.

Input	Units	Value
Seeds	kg/ha	5
Ν	kg/ha	200
Р	kg/ha	100
Κ	kg/ha	200
Pesticides	kg/ha	0
Herbicides	kg/ha	0
Diesel	kg/ha	48.1
Output	Units	Value
Achenes	kg/ha	1124
Residual lignocellulosic biomass	kg/ha	9675

Table 2. Input and output data for cardoon cultivation [19].

The soil was prepared for the plant with basic fertilization (carried out twice in the first year), followed by intense tillage (deep plowing and harrowing). The thistle seedlings, which were previously obtained in a seedbed, were then transplanted into the ground, with a density of 1 plant/m<sup>2</sup>. After the first year of cultivation, the thistle was grown for two years in order to reach its full production potential. At the end of the third year, the production was 12.9 t/ha (corresponding to about 9675 t/ha of residual biomass) in non-irrigated standard conditions. The epigean biomass was only collected once in the third year, at the end of the summer, and it was stored in round bales. All of the agronomic data come from experimental measurements that were carried out directly in the field and are, therefore, primary data. Only the data on the average fuel consumption used for carrying out agricultural operations in the field were obtained by considering the average values of agricultural machines' consumption that were obtained from the sector literature and are, therefore, secondary data.

The transport of residual thistle biomass from the field to the biorefinery plant was modeled by imagining transporting the biomass with a truck with a maximum load capacity of 40 t (27 t load) over a distance of 100 km return. This distance was arbitrarily fixed while taking a series of parameters into account: (1) maximum distance of 70 km in the supply of biomass for energy use (support scheme for the short supply chain in Italy); and, (2) upper limit of 100 km to ensure the economic convenience of the supply chain. Table 3 shows the inventory relating to the transport step.

Input	Units	Value
Distance (return)	km	70-100
Transportation efficiency	MJ/(t km)	0.94
Emission factor of the fuel	kg <sub>CO2eq</sub> /MJ	0.08764

Table 3. Input data for cardoon transportation.

The biorefinery phase was modeled when considering all of the material and energy inputs of the individual process operations (subunits) in its optimized configuration, according to the layout in Figure 1. Table 4 shows an example of the inventory data relating to a main process step as the pretreatment steam explosion. Except for the first and last subunits, the outflows from each subunit represent incoming flows for the next subunit, with a consequent cancellation of the effects in terms of the release of emissions into the atmosphere and water consumption.

Units	Value
1 4	-
kg/h	7486
kg/h	76
kg/h	6362
kg/h	6240
kWh	192
Units	Value
kg/h	17,884 (5344 dry)
kg/h	1272 (1018 dry)
	Units kg/h kg/h kg/h kWh Units kg/h kg/h

**Table 4.** Input and output data for the steam explosion pretreatment process.

#### 3. Results and Discussion

This paragraph shows the main results of the cardoon-biorefinery assessment in terms of material balances, energy balances, and environmental impact.

#### 3.1. Material Balances

Table 5 shows the material balances of the optimized biorefinery. Total material flowrate, water flowrate, and other compounds (e.g., sugars, BDO, enzymes, CO<sub>2</sub>, etc.) were calculated based on elaborations and process simulations that are described in the previous paragraphs.

	Flowrate	Water	Others
Residual cardoon material	7485	1123	6362
H2SO4 + water	5316	5240	76
Hemicellulose	8043	7560	483
Fiber + cellulose	16,888	15,727	1161
E-CO <sub>2</sub>	117	0	117
Enzymes	94	0	94
Organic waste	1600	1349	251
Hydrolysis cake	3813	1525	2288
Hydrolyzed cellulose	23,882	21,755	2127
Biogas	237	0	237
Sludge	2567	0	2567
Wastewater	2798	2798	0
W-CO <sub>2</sub>	22	0	22
2GS	5276	2666	2610
F-CO <sub>2</sub>	988	45	943
BDO rich	4657	2670	1987
BDO	1001	3	998

Table 5. Material balances for the main process streams (kg/h).

In particular, a 1,4-BDO global yield that is equal to 15.7%wt, dry was derived from the process simulation. This was coherent with previous finding by Forte et al. [12] (16.1%, using wheat straw as feedstock) and Satam et al. [16] (23.9%, using glucose derived by corn stover).

The largest CO<sub>2</sub> flow that was derived from the BDO fermentation process (943 kg/h); this, together with CO<sub>2</sub> from enzymes production and wastewater treatment sections, makes a total amount of direct CO<sub>2</sub> emission of 1060 kg/h (yield to CO<sub>2</sub> = 17%).

The burned material (hydrolysis cake and biogas) was 40% of dry feedstock, producing steam and power by the cogeneration section.

Unconverted sugars, unrecovered BDO, and other impurities were mainly recovered in the sludge.

#### 3.2. Energy Balances

The overall electricity demand was equal to 11,163 MWh/year, whose percentage distribution between the different phases of the process is shown in Figure 3a. The total installed power was 1732 kW.



Figure 3. Distribution of electricity (a) and thermal (b) needs (MWh/year).

Over half of the total electricity requirement was due to the in situ production of enzymes, which was mainly due to the aeration of the enzyme broth during biological growth and the separation of the enzymes utilizing membrane-based technologies.

As far as thermal energy was concerned, the entire production process requires approximately 93,607 MWh/year, distributed as:

- 16,280 MWh/year for process steam at a pressure of 25-barg.
- 39,522 MWh/year for process steam at a pressure of 14-barg.
- 28,501 MWh/year per 10 barg pressure steam cycle.
- 9302 MWh/year for hot water (70 °C).

In percentage terms, the demand for thermal energy was divided into percentage between the different phases of the process, as shown in Figure 3b.

The energy recovery system has been designed to almost completely cover the entire energy requirement of the BDO production process. According to the process's capacity to produce biogas and solid fuel (respectively, 236 kg/h and 3813 kg/h), the obtainable net power was equal to 1091 kWe, of which 375 kWe come from the internal combustion engine and 716 kWe from the turbine steam

powered. Despite the lower supply of electricity, the energy recovery system can cover around 78% of the total electricity demand, generating around 8724 MWh/year out of 8016 h/year. Figure 3a shows the estimates on the electricity balance, divided by the different phases of the process.

Instead, the thermal energy recovery system was able to entirely satisfy the overall demand of the sugar production process, while BDO purification columns require a high-pressure steam. In total, 84,064 MWh/year were produced against the 77,325 MWh/year + 16,280 MWh/year (for process steam at a pressure of 25 barg) were required. Consequently, the thermal energy recovery system can cover around 83% of the total thermal demand. The back pressure steam turbine produces about 11,650 kg/h of steam at a pressure of 14-barg. Of these, approximately 6363 kg/h were used for the steam explosion pretreatment; another 4600 kg/h were decompressed to 10-barg of and then used to concentrate sugars. In order to vaporize the BDO/water mixture in the distillation column's reboiler, 2.0 MW were necessary, corresponding to 16,280 MWh/y at 200 °C (high-pressure steam). This high-pressure steam was considered to be derived by an external fossil source because the cogeneration plant in situ could not produce it. The rest of the steam flow was used to produce hot water. The biogas cogeneration system also produces an additional flow of hot water.

In terms of water consumption, the total amount of "clean" water (tap water) that was required for the process was estimated at 27,089 kg/h and 21,022 kg/h recycled through the wastewater treatment section. Therefore, the overall system configuration has a net freshwater requirement of 6067 kg/h, corresponding to 48,633 tons/year. The cooling water amount to use for the distillation column condenser was equal to 186.4 t/h (recycled). Regarding fuel consumption, on the whole, 113,106 L/year of diesel was consumed by the cultivation process. In conclusion, while using the residual material as a solid fuel for the energy recovery system, it has been estimated that it was possible to achieve complete self-sufficiency for the thermal energy demand.

#### 3.3. Environmental Impact

The functional unit, which was given by the quantity of product taken as a reference for the impact analysis, was defined to be equal to 1 kg of BDO produced by the cardoon-based biorefinery. The system's boundaries were represented by the solid line of Figure 4 and it included the three phases mentioned above.

The emissions that are linked to the transport and cultivation phases added to the emissions associated with the processing in the biorefinery plant (0.813  $kg_{CO2eq}/kg_{BDO}$ ) provide an overall value of 2.82  $kg_{CO2eq}/kg_{BDO}$ .

For the biorefinery step, the biggest environmental impact was derived by the fermentation and BDO purification section. This was because the required thermal energy for the 2GS production was considered to be possible to produce by the cogeneration plant burning residue materials.

The carbon footprint value that was calculated for the entire production process of BDO was equal to 2.82 kg<sub>CO2eq</sub>/kg<sub>BDO</sub>. The cultivation phase contributes with 1.94 kg<sub>CO2eq</sub>/kg<sub>BDO</sub>, the transport phase has very little impact, only for 0.067 kg<sub>CO2eq</sub>/kg<sub>BDO</sub>, while the biorefinery phase contributes 0.813 kg<sub>CO2eq</sub>/kg<sub>BDO</sub>.

Figure 5 shows the specific environmental impact due to four different BDO production phases. Cultivation has the biggest impact (1.94  $kg_{CO2eq}/kg_{BDO}$ ). The purification of BDO presents the second biggest impact (0.61  $kg_{CO2eq}/kg_{BDO}$ ) due to the utilization of high-pressure steam in order to sustain the distillation column reboiler. The 2GS production has an impact that is equal to 0.20  $kg_{CO2eq}/kg_{BDO}$  for the concentration and enzyme production steps. Transport represents the last one.

#### 3.4. Comparison between the Environmental Impact of Biorefineries

In a previous work [12], assessing 1,4-BDO from wheat straw, the final climate change impact in terms of equivalent  $CO_2$  was equal to 1.6 kg<sub>CO2eq</sub>/kg<sub>BDO</sub>, where the cultivation phase had an impact of 0.16 kg<sub>CO2eq</sub>/kg<sub>BDO</sub>. This different value can derive from a different evaluation of the input of energy and material to the cultivation phase, in terms of nutrient requirements.



Figure 4. Boundaries of the system considered in the environmental analysis.



**Figure 5.** Distribution of environmental impact of cultivation, transport, 2GS production, BDO production phases.

The work of Adom et al. [49] reported minimum emissions to produce 1,4-BDO equal to approximately 2.5  $kg_{CO2eq}/kg_{BDO}$ , but through bioprocesses corn stover to succinic acid to 1,4-BDO routes.

The present case study highlighted a general reduction of impacts of the bio-based BDO with respect to the fossil counterpart that is equal to  $4.4 \text{ kgCO}_{2eq}/\text{kg}_{BDO}$  [12]. In terms of CO<sub>2</sub> emissions per GJ, the present study found 98 kg<sub>CO2</sub>/GJ for emissions due to 1,4-BDO production. The value of impact equal to 98 kg<sub>CO2</sub>/GJ<sub>BDO</sub> is comparable to other biobased products as first-generation bioethanol

(218 kg<sub>CO2</sub>/GJ), biodiesel (144 kg<sub>CO2</sub>/GJ) [50], second-generation bioethanol (17 kg<sub>CO2</sub>/GJ) [51], and biomethanol (215 kg<sub>CO2</sub>/GJ) [7], but lower.

In this paper, a process layout for the production of biobased product through the sugar platform way simulated at the industrial scale. The direct use of cardoon biomass for energy production through combustion can be an alternative option for the full exploitation of local biomass. Combustion is a well-developed and robust technology and it has been applied to several feedstocks. On the other side, some investigations from Abelha and co-workers [52] demonstrated that the utilization of cardoon in combustion plants would require a preliminary densification into a pelletized form in order to avoid problems with the feedings. Furthermore, the authors concluded that the mono combustion of cardoon without the addition of woody type biomass could pose problems at an industrial scale in fluidized bed, due to the high levels of HCl and  $NO_x$  emissions and bed agglomeration problems. Finally, stable support schemes and subsides remain the key factor for the biomass deployment beyond 2020 for the deployment of bioelectricity and bioheat. Some estimations can help to compare the thermochemical valorization of cardoon with the conversion to value-added biobased product. When considering a plant treating capacity of 60'000 t/y, a LHV of cardoon of 17 MJ/kg<sub>DRY</sub>, a typical power efficiency of 25% [53], an annual production of 240'000 MWhe/y can be estimated corresponding to 79'704  $t_{CO2}$ /y of direct emissions, namely 307 kg<sub>CO2</sub>/GJe. This indicates that the valorization of cardoon by 2GS and BDO process pathway has a lower environmental impact than the thermal process pathway. Recent market analysis indicated that the market size for 1,4 butanediol, in terms of value, is projected to reach \$8.96 Billion by 2019, registering a CAGR of 8.23% between 2014 and 2019 [54]. Additional benefits of the novel layout that are presented in this paper include the high versatility of the sugars platform, since it can be virtually used for the production of many alternative biobased products.

The biorefinery system is a quite complex concept and a reliable assessment of the most promising bio-based production pathways needs to encompass all of the technical barriers as well as wider sustainability related to environmental, economic, and social issues [55]. The current trend of converting traditional fossil-based products to bio-based should be explored and proceed with caution, even if the bio-based products are generally recognized as less energy and GHG emissions intensive [56].

When coupling the increased interest in producing bio-products from vegetable oil, bio-products from lignocellulosic fractions (residues), and the large production of biofuel from biomass, a scenario in which the feedstock biomass becomes scarce is not farfetched [57]. From a decision making point of view, GHG emissions and fossil fuel consumption will be meaningless quantities if there are not enough natural resources to go around. For this reason, it is extremely important to address the sustainability issue while taking the depletion of the natural resources and the increase deteriorating state of natural ecosystem into account.

The results appeared to confirm the potential of lignocellulosic residues of cardoon as feedstock for further effective processing within regional bio-based production chains. Nevertheless, the availability of this materials is driven by other critical points, usually identified, as follows:

- economic convenience of the production of oil from thistle grown up in marginal lands; and,
- potential competition with other high-added value compounds potentially produced from a lignocellulosic feedstock.

The possible improvements can be applied to the entire supply chain; these include optimized management of the cultivation phase (less use of nitrogen fertilizers, less use of fuels, carbon capture, and storage) and greater attention to saving and energy recovery in the biorefinery phase.

#### 4. Conclusions

In this work, a cardoon based biorefinery producing bio-BDO from the lignocellulosic fraction was studied. A plant processing 60 kton/year of residual biomass to achieve 8.0 kton/year of BDO has been modeled. Cultivation, transport, second-generation sugars (2GS) production, and final BDO production and purification were considered.

The process layout was defined and optimized. The plants were sized and, for each process step, the main flows of materials and energy were identified and described in order to provide the related financial statements. A simplified environmental impact analysis was applied to the entire supply chain in order to assess the carbon footprint.

The results showed that the production of BDO is self-sustaining and that approximately 78% of the total electricity demand can be achieved by converting the secondary streams. Instead, the thermal energy recovery system is able to satisfy the overall demand of the sugar production process entirely, while the BDO purification columns require high-pressure steam. The thermal energy recovery system can cover around 83% of the total thermal demand.

The overall contribution to greenhouse gas emissions from the production of BDO equal to  $2.82 \text{ kg}_{\text{CO2eq}}/\text{kg}_{\text{BDO}}$  was obtained, which was comparable to other biobased products, but lower than conventional case of solid biomass combustion.

The final aim of a quantitative assessment of a novel biorefinery layout with the potential for being integrated in an existing vegetable oil-based value chain from cardoon has been achieved. A cardoon value chain can represent the great use for developing new models of integrated supply chains and suggests new developments and insights.

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