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Sustainability of Biorefineries: Challenges and Perspectives

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Abstract: Biorefineries have been defined as complex systems where biomass is integrally processed to obtain value-added products and energy vectors, involving recent research advances, technological trends, and sustainable practices. These facilities are evolving since new pathways and challenges for biomass upgrading appear constantly aimed at increasing process sustainability. Nevertheless, few literature papers summarize how these new trends can improve biorefinery sustainability and boost the transition to renewable resources. This paper reviews several challenges and future perspectives before biorefinery implementation at the industrial level. Challenges related to waste stream valorization, multifeedstock use, biorefinery energy matrix diversification, and new products based on new biomass conversion pathways are reviewed. Thus, this paper provides an overview of the most recent trends and perspectives for improving biorefinery sustainability based on waste stream minimization, integral use of raw materials, and high-value bio-based compound production. A case study is discussed to show how integral biomass upgrading can improve the economic and environmental performance of existing processing facilities. Carbon dioxide capture, storage, and conversion, as well as energy matrix diversification, have been identified as the most important aspects of improving the environmental performance of biorefineries (decarbonization). Moreover, multifeedstock biorefineries are profiled as promising options for upgrading several biomass sources in small-scale and modular systems to produce value-added products for boosting rural bioeconomies. Finally, new ways to produce more bio-based products must be proposed to replace existing oil-based ones.

Keywords: bioeconomy; biomass upgrading; carbon dioxide capture; decarbonization; multifeedstock biorefinery; process design

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1. Introduction

Biomass is one of the most important renewable resources used as an alternative to producing different value-added products and energy vectors [1]. The increasing trend in biomass use is attributed to the environmental damage caused by the excessive use of fossil fuels. Different processing lines have been developed to upgrade biomass and organic sources [2,3]. Biorefineries have been profiled as promising alternatives to upgrade all biomass components for different productive sectors. These facilities are key to promoting sustainable development and bioeconomy implementation in different regions since biomass is a renewable resource available worldwide [4]. Biorefineries have been researched and designed many years ago. Few biorefineries have been implemented as greenfield or brownfield processes. Moreover, the product portfolio provided by the existing installed facilities can be increased since most biomass processing plants are addressed to produce energy vectors (i.e., biogas, biodiesel, bioethanol), some value-added products (e.g., levulinic acid, bioplastics), and bioenergy (heat and power) [5]. Therefore, new processing lines, strategies for growing biomass upgrading at the industrial level, and pathways for increasing the technological readiness level (TRL) must be researched to boost biorefinery implementation [6]. Nevertheless, few literature papers summarize different trends for boosting biorefineries implementation.

Sustainability has been defined as the perfect balance between economic, environmental, and social dimensions [7]. Furthermore, different perspectives have been added to the sustainability concept involving political, technical, and safe and security aspects [8]. Sustainability was embodied in the so-called "Sustainable Development Goals—SDGs", which are targeted to reduce poverty, increase the quality of life, decrease natural resource pollution and depletion, and create a more equitable, advanced, plural, and fair society [9]. Several pathways and strategies have been proposed to accomplish the SDGs [10–12]. One of these ways is using biomass as renewable raw material instead of crude oil by implementing new technologies and efficient processes. In this sense, biorefineries are sustainable by definition. However, real biomass upgrading facilities must guarantee the maximum socio-economic performance, while minimizing the environmental impact. Thus, different challenges such as (i) waste stream minimization, (ii) energy matrix diversification, (iii) multifeedstock use, and (iv) new products proposal must be reviewed and discussed as alternatives to be considered when designing and implementing biorefineries. However, these challenges have been addressed in a stand-alone way without integration under a holistic vision for increasing biorefinery sustainability.

Biorefinery sustainability can be increased by applying mass and energy integration criteria. For instance, fermentation processes have been improved by designing simultaneous saccharification and fermentation (SSF) processes [13]. Fractional conversion of equilibrium-based reactions (e.g., esterification) has been increased by designing reactive-extraction processes [14]. These new processing pathways are available to be implemented when designing biorefineries. Nevertheless, high economic costs are required limiting the possible implementation at the industrial level. Even so, biomass upgrading processes and biorefineries are evolving constantly to find new ways to minimize residues, increase products portfolio, and upgrade all biomass fractions [15]. For example, ozonation has been studied as an efficient way to decrease the chemical oxygen demand (COD) of anaerobic digestion effluents [16]. Furthermore, microorganisms have been studied as potential options for improving substrate consumption [17]. Thus, the research and development of new trends for increasing biorefinery sustainability is worthy of discussion since these trends can make biorefinery implementation in different world regions more possible. Moreover, new trends are addressed to decarbonization goals, energy transition, and bioeconomy.

Industrial biomass conversion facilities are addressed to produce energy vectors such as bioethanol and butanol using microorganisms such as *Saccharomyces cerevisiae* and *Clostridium acetobutylicum* [18,19]. These processes still require improvements due to waste streams being produced without any further valorization (stillage and carbon dioxide). In this way, different processes have been researched to improve techno-economic and environmental performance. Carbon dioxide capture and valorization, stillage upgrading, new catalytic processes for upgrading biomass, solar-photovoltaic energy implementation in processing plants, and different raw materials upgrading are examples of the most recent trends proposed for increasing biorefinery sustainability. These trends have been profiled as potential alternatives for increasing biorefinery sustainability since these trends can be applied to existing biomass upgrading plants. For instance, the potential use of stillage for producing energy through anaerobic digestion has been assessed to increase bioethanol-producing plant sustainability [20]. Heterogeneous catalysis has been researched to increase product portfolio and yields in thermochemical processes [21]. Nevertheless, few literature papers have reviewed and discussed how these trends can improve biorefinery sustainability since implementing these processes affects the technical, economic, environmental, human, and social dimensions. In this way, this paper reviews challenges and future perspectives before biorefineries implementation at the industrial level. Challenges related to waste stream valorization, multifeedstock use, biorefinery energy matrix diversification, and new products based on new biomass conversion pathways are reviewed. Thus, this paper provides an overview of the most recent trends and perspectives for improving biorefinery sustainability based on waste stream minimization, integral use of raw materials, and high-value bio-based compound production.

Regarding the above context, the novelty of this paper is addressed to highlight some of the most important challenges and perspectives for developing and implementing sustainable biorefineries based on new trends for biomass upgrading and waste minimization. The aim of this manuscript is to provide a review of different challenges and perspectives for biorefinery sustainability increase through the following sections (i) overview of the biorefineries concept. (ii) existing processes applying the biorefinery concept, (ii) sustainability assessment of biorefineries, (iv) trends for improving biorefinery sustainability, and (v) cases of study of sustainable biorefineries, (vi) challenges and perspectives for implementing future biorefineries.

2. Biorefineries: Concept, Design, and Assessment

2.1. Biorefinery Concept

Several definitions and points of view about the biorefinery concept have been considered by a number of authors and organizations (see Table 1). Depending on the stakeholders involved, the biorefinery definition can vary [22]. One way to see biorefineries is as an integrated processing center for biomass upgrading. As a result, a biorefinery is a facility designed to transform biomass into various products including chemicals, energy sources, and high-value compounds. This brief explanation leaves aside key aspects such as sustainability, efficient raw material utilization, and multiprocessing. In order to understand various viewpoints, several biorefinery definitions should be reviewed. Table 1 lists some of the most important biorefinery definitions given in recent years.

The concepts in Table 1 demonstrate an evolution of the biorefinery notion. The definitions of a biorefinery distinguish between energy, bio-energy, and value-added products. The upgrading of biomass into bulk, specialized, and fine chemicals occurs in sophisticated systems known as biorefineries. In order to prevent generalization and misunderstanding across many scientific community partners over time, the evolution of the biorefinery concept is provided. The idea of a biorefinery should also incorporate significant sustainable design elements. Not all methods for upgrading biomass are considered biorefineries. However, all biorefineries are simply methods for upgrading biomass. As a result, the biorefinery idea must include sustainability as an integral component.

The idea of a biorefinery is comparable to oil-based refineries, which produce a variety of chemical compounds that can be upgraded into a wide range of end-products. A biorefinery utilizes the majority of biomass elements to add value to the raw materials treated [23]. Two factors allow us to differentiate between oil refineries and biorefineries. The raw materials themselves are the first aspect. Biomass components are fresh raw materials that have no impact on the carbon cycle (as in the case of fossil fuels). The second factor is related to the technologies. Oil refineries have the expertise to alter and enhance raw materials. On the other hand, efforts are being made in research and development to progress knowledge about the various ways to add value to biomass sources. Moreover, biorefinery technologies are more complex since biological products require more specialized processing conditions (i.e., temperature, pressure, pH, salt concentration). Bulk, specialty, fine chemicals, energy vectors, and power are all produced by a biorefinery. From there, various academics have predicted the high potential of biomass as the new raw material to support and launch a bio-based economy in the future.

The definitions included in Table 1 serve as the starting point for recognizing the intention of a biorefinery. These goals include maximizing the value of biomass resources, producing competitive and marketable goods and services, reducing the environmental impact caused by excessive fossil fuel use, promoting a sustainable future through non-oil-based processes, and acting as a medium for developing the bio-based economy. Biorefineries can be compared to those processes addressed to upgrade crude oil. Nevertheless, biorefineries involve more complex tasks since efforts must be made to overcome existing and future issues related to raw material conversion and technological invention.

Table 1. Biorefinery definitions given in the open literature.

Authors	Biorefinery Concept	Refs.
International Energy Agency—Task 42	Sustainable processing of biomass into a spectrum of marketable products and energy	[24]
US Department of Energy (DOE)	A biorefinery is an overall concept of a spectrum of valuable products based on the petrochemical refinery	[25]
National Renewable Energy Laboratory	A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic biobased industry	[7]
Huang, H.J.; Ramaswamy, S.; Tschirner, U.W.; Ramarao, B. V	A biorefinery is a set of processes that use bio-based resources such as agriculture or forest biomass to produce energy and a wide variety of chemicals and bio-based materials, similar to modern petroleum refineries.	[26]
Moncada, Aristizábal, and Cardona	A biorefinery is a complex system where biomass is integrally processed or fractionated to obtain more than one product, including bioenergy, biofuels, chemicals, and high value-added compounds that only can be extracted from bio-based sources after an accurate design	[1]
Ganti S. Murthy	A biorefinery is defined as a facility/cluster of facilities for processing biobased feedstocks into valuable products addressing the needs of diverse markets for fuels, feed, plastics, and other commodity chemicals in a sustainable manner.	[25]

According to the most recent definitions provided by Moncada et al. [1] and Murthy [27], a biorefinery can be seen as a complex system where several processes are brought together. Biorefineries upgrade all biomass components to create various products that can be sold domestically and abroad. Most of the biorefineries described in the literature are still in the conceptual design stage, which illustrates how challenging it is to put a genuine facility into operation. However, Cardona Alzate et al. [28] cite a few biorefineries that have been set up in North America and Europe. Most biomass components are not utilized in biomass existing biomass processing facilities, but biorefineries can enhance and improve sustainability following the biorefinery principle. It is challenging to find procedures that upgrade all biomass constituents. Finally, biorefineries must be sustainable by definition. This statement involves a good performance from economic, environmental, human, and social perspectives [7].

2.2. Biorefineries Design

Biorefineries are designed considering several aspects such as raw materials, technologies, and products. Different biorefinery design approaches have been proposed and studied for upgrading biomass sources. The most common design approaches are (i) optimization and (ii) conceptual design. These approaches have been used by different authors for proposing and evaluating biorefineries [28,29].

2.2.1. Optimization Approach

The optimization design methodology aims to maximize either mass yield, energy consumption, or economic potential considering several limitations related to chosen technology, conversions, reactants, and products [1]. Moreover, this approach involves the minimization of waste streams for increasing sustainability. The first step to designing a biorefinery applying this method is to formulate the optimization problem (e.g., maximize the profit margin or minimize production costs) [30]. This step involves the formulation of an objective function based on restrictions and the desired objective. This equation is obtained after identifying all the variables involved in the system (i.e., biorefinery). Currently, multi-objective optimization problems have been proposed to guarantee the sustainability of the process [29]. An overall review of the available processes and technologies of the biomass upgrading process (i.e., pretreatment, reaction/transformation, separation, and product recovery) is required to perform a comprehensive analysis of the possible conversion routes. In this step, the so-called superstructure is created. The next step involves the solution of the formulated problem considering the mass and energy balances of each of the unit operations involved in the superstructure.Optimization software is required to evaluate the biorefinery system. For instance, GAMS is one of the most used packages to develop this work [31–33]. Pongpat et al. have reported an optimization process for improving the economic and environmental performance of a sugarcane-based biorefinery involving new products. This study (among others) demonstrates the potential of the use of software to enhance biorefineries performance.

The optimization methodology is focused on finding the best process configuration through the simultaneous evaluation of different aspects. In other words, this methodology tries to give the best biorefinery configuration through a comprehensive integration and evaluation of several technologies implied in different stages. Moreover, the optimization approach seeks to set the basis of the techno-economic analysis by evaluating an objective function. Nevertheless, Cardona Alzate et al. [28] highlighted one of the main drawbacks of the optimization design approach. This drawback involves technologies with low technological readiness levels (TRL) in the superstructure. Thus, the optimal configuration can be proposed based on unproven processes at the industrial scale, limiting the real implementation of these facilities. Therefore, one way to improve this design methodology is through the consideration of only well-established technologies.

2.2.2. Knowledge-Based Approach/Conceptual Design

The knowledge design approach or conceptual design methodology is a way to design biorefineries based on a holistic vision, including all aspects related to biomass upgrading from a process engineering perspective until the inclusion of social elements to develop a biorefinery able to improve local, regional, national, and international issues. This design methodology can be considered an adaptation of the traditional conceptual design approach of chemical facilities in the last years [34].

The first step in a biorefinery design process is selecting the raw materials and products based on chemical composition, seasonability, availability, market price, and demand criteria. Then, different restrictions ought to be considered according to the applications and use today. The production of high-value-added products such as specialty chemicals and fine chemicals is favored over bulk chemicals (e.g., energy vectors). These high value-added products include functional foods, metabolites, antioxidants, probiotics, and vitamins, among others. Once the selection of raw materials and products has been made, the choice of technologies and conversion pathways is required.

The conceptual design approach includes three types of analysis, (i) technical, (ii) economic and, (iii) environmental as well as two types of integration, (i) Mass, and (ii) Energy [35]. Nevertheless, the main advantage of this methodology is related to the inclusion of strictly-conceptual aspects. The conceptual design approach can consist of a social analysis, which is strictly necessary to refer to the sustainability concept. The conceptual design can be seen as an integral way to perform a biorefinery design. In contrast to the optimization design approach, a superstructure is not formulated in the knowledge-based approach because the technologies and process configurations are specified based on the hierarchy, sequencing, and integration concepts.

The hierarchy concept considers raw materials as the first level of a biorefinery system. Depending on the studied feedstocks, several products can be obtained. Thus, a portfolio of products and chemical platforms can be predefined based on the composition of the raw material (e.g., sugar alcohols, organic acids, food products). Raw materials (i.e., feedstocks) can be classified as first, second, and third generation. First generation raw materials are related to biomass from crops (e.g., corn, sugarcane, wheat, and sugar beet).

Second generation raw materials are residues from crops, agroindustry, and non-edible crops. Finally, third generation raw materials are related to microalgae and macroalgae [28]. Cherubini et al. [24] proposed eight families of products, which can be produced using biomass sources (i.e., fertilizers, biohydrogen, glycerin, chemicals and building blocks, polymers, food, animal feed, and biomaterials). The second hierarchy level is technology. The hierarchy concept is focused on the step that affects each process, which is a modification of the onion diagram [34]. The critical stage of a biorefinery can vary depending on the desired platform. The direct relationship between raw materials and products to be obtained is overcome by introducing the multifeedstock biorefinery concept. These biorefineries are defined as processes with more than one feedstock [36]. Nevertheless, this kind of process is relatively new because of the low number of publications associated with the topic. Thus, multifeedstock biorefineries can be classified as a possible trend to improve biorefinery sustainability [37].

The sequencing concept considers a logical order and relationship between biomass upgrading technologies and the desired products [38]. Thus, the products' portfolio in a biorefinery must be defined before deciding on the technologies involved in the process. Moreover, the sequencing concept applies the knowledge of different conversion technologies, raw materials, and products. This step is based on the experience of the designer (know-how). Finally, the sequencing concept involves the precise definition of the goal and scope of the biorefinery to achieve a more accurate design [35]. The integration concept seeks to improve the biorefinery design through the implementation of mass and energy integration. Therefore, mass and energy balances are the essential information to be considered in this stage of the process design. For this, the use of simulation tools is recommended. Mass integration can refer to (i) decreasing raw materials demand, (ii) recycling process streams, (iii) combining unit operations, and (iv) intensifying processes. On the other hand, energy integration focuses on designing a heat exchange network or the implementation of power cycles to improve the efficiency of each stage in the biorefinery [39].

Finally, sensitivity analysis is necessary to identify the biorefinery trends in terms of economic and environmental aspects. The sensitivity assessment of a biorefinery system can be conducted considering different perspectives. For instance, a variation of the processing scale, raw materials costs, product costs, conversion, and yields can give a more sustainable biorefinery. The information provided by the sensitivity analysis can serve to define aspects related to the scale of the process [40], the best process configuration [41], and net economic revenues [42]. Examples of sensitivity analysis reported in the open literature are related to (i) processing scale, (ii) minimum selling price, (iii) minimum production costs, (iv) profit margin, and (v) carbon footprint.

Biorefineries have a high potential to integrate different value chains due to the production of several compounds. Nevertheless, most facilities designed and proposed in different research projects as well as strategies for upgrading residues produced in industrial facilities have not been implemented at the industrial level. Few real biorefineries are operating in Europe and America compared to the existing oil-based processes [43]. These biorefineries are based on the total use of the raw material for producing several products. An example of these existing biorefineries is sugarcane mills since these facilities produce sugar, heat, and power. On the other hand, other processes so-called conventional biorefineries are related to (i) pulp and paper mills, (ii) palm oil mills, and (iii) corn mills [44]. These existing plants have approached the biorefinery concept over the years since new technological improvements have been implemented for decreasing environmental impact and reducing operating costs. Indeed, cogeneration units have been implemented as an alternative for self-generation.

First-generation raw materials are being used for producing marketable products and replacing oil-based compounds. For instance, Galatea-BioTech company (Italy) is producing polylactic acid (PLA) using corn as raw material, Novamont is producing fully biodegradable and compostable bioplastics (Mater-Bi) using renewable feedstocks, and GF Biochemicals is producing levulinic acid and derivatives (esters and ketals) from renewable feedstocks [5]. There are other companies addressed to produce bio-based products. These examples are reviewed by Cardona Alzate et al. [28], Solarte-Toro et al., [5], and the Biorefineries Consortium [45]. These companies are the first step toward biorefineries implementations since the economic feasibility is being demonstrated. Thus, large and industrial facilities can be developed using renewable raw materials. In this way, the biorefinery concept can help to boost a bio-based economy based on sustainability principles. All these above-mentioned biomass upgrading processes are considered brownfield processes (i.e., existing plants).

Greenfield biorefineries (i.e., new plants) have not been widely introduced since these projects require high capital investments from the private sector and government. Even so, biofuels producing plants (i.e., biodiesel, biogas, and bioethanol) are considered the basis for the implementation of future biorefineries. The present movement to transition away from an oil-based economy is accelerating conversion efforts across all industries [46]. Then, in order to prevent concerns with food security and energy transition, bioeconomy establishment methods are being implemented to encourage the use of second-generation raw materials rather than first-generation sources. Biorefineries help build the bioeconomy and the shift to renewable energy sources.

3. Sustainability Assessment of Biorefineries

In order to pursue an improved quality of life, social, economic, and environmental factors must be balanced. This is the sustainability notion. In light of this, the term "sustainability" should be used to refer to a long-term objective and the ideal state of a system (e.g., a chemical process, a biorefinery, or a city). The sustainability idea depends on the end result obtained after a number of system improvement techniques have been used. Regarding the previous description, the term sustainability is a multidimensional and integral idea because different factors must be considered. From this, the economic, environmental, and social factors are the most accepted to define sustainability. Hence, these factors are known as the three pillars of sustainability, three dimensions of sustainability, or triple bottom lines (TBL) [47,48]. These dimensions are the basis to determine if a system can be defined as sustainable or not. Nevertheless, recent discussions about the sustainability concept is involving the human/culture dimensions. For instance, Sabatini (2019) explores the relationship between the TBL and the fourth dimension [49]. The human/culture dimension has not been sufficiently explored since there are no quantitative methods for assessing this dimension. The authors of this paper focus only on the TBL since most of the recent studies are addressed to quantitatively estimate the sustainability of biorefineries and processes [50,51].

The environmental dimension involves ensuring a controlled consumption of natural resources such as materials, energy sources, land, and water. Syed and Tollamadugu define this dimension considering the rate of renewable resource harvest, environmental pollution increase, and non-renewable resource depletion carried out indefinitely [52]. This dimension has been assessed by using different methodologies. Currently, the environmental dimension is assessed by applying the life cycle assessment methodology defined by ISO14040 [53]. For instance, Joglekar et al. estimated the environmental performance of a fruit peel waste biorefinery for producing bioactive compounds, essential oils, and energy vectors [54]. Similarly, Solarte-Toro et al. assessed the environmental performance of a small-scale biorefinery system for upgrading avocado residues into a series of marketable products [55]. These studies allow for identifying hotspots in a process or an entire value chain and proposing new ways for improving [56].

The economic dimension is defined as the permanent capacity of an economic model to satisfy all human needs through the goods and services provided without risking the material resource of a group of investments [7]. An economic system should supply a product required by customers and consumers at reasonable prices, considering both cover production costs and provide a profit margin concerning the initial investment. The economic dimension also involves the correct and efficient use of the finite resources used in a productive chain to produce an operational profit and avoid economic losses. The economic dimension is assessed to find financial parameters such as net present value (NPV), internal rate of return (IRR), and payback period (PBP). Moreover, this assessment is addressed to determine operating and capital expenditures [57]. There are sufficient literature reports reporting economic assessment of different biorefinery systems [37,41,58]. Thus, the authors consider that examples are unnecessary. Nevertheless, economic assessment accuracy is a crucial factor to obtain reliable values related to investment and revenues. Thus, Rueda-Duran et al. proposed a new strategy to improve the economic assessment of conceptual design biorefineries by combining basic and detailed engineering aspects [59]. These authors applied the strategy to find costs for producing poly-lactic acid using different second-generation raw materials (e.g., plantain, sugarcane bagasse).

Finally, the social dimension is conceived as a process to promote well-being. Thus, the social dimension involves different aspects of health, work, quality of life, social security, and an affordable and reliable provision of essential elements to guarantee society's development (e.g., education) [60]. The social dimension combines political and cultural aspects, which are the base of today's societies, and integrates these aspects with the physical environment. From this integration, the social dimension encompasses and studies topics related to cultural life, social amenities, and citizen participation systems, promoting society maturing through the evolution of people and places. Finally, the social dimension can be perceived and reached, supporting current and future generations' ability to create functional, healthy, and organized populations by establishing formal and informal processes, systems, and structures. This ability will provide equitable, diverse, connected communities and offer a good quality of life. Nevertheless, the social dimension has not been analyzed for biorefinery systems since quantitative indicators were missing. In the last years, the research for improving biorefinery sustainability proposed a list of quantitative and qualitative indicators for measuring the social impact of a process, product, or value chain. These indicators are reported in the Product Social Impact Life Cycle Assessment (PSILCA) database developed by GreenDelta [61]. These indicators have been applied to analyze biorefineries addressed to produce hydrogen and bioethanol [62,63].

The sustainability dimensions are evaluated in the same way to ensure an inclusive assessment of any system considering all aspects. Therefore, similar methodologies (e.g., life cycle assessment) should be used for this purpose [64]. Moreover, the three dimensions involve a series of guidelines, parameters, conditions, and statements to determine the behavior of a system from each perspective. The economic, environmental, and social dimensions are dependent due to the complex development of our society. The sustainability concept is represented in Figure 1. This figure is a Venn diagram, which shows the multidimensionality and integrality of the sustainability concept. The three dimensions are present, as well as the inherent relationship between them. This representation of the sustainability concept allows understanding the sustainability assessment to be an integral evaluation of a system considering complex aspects such as socio-ecology, socio-economy, and eco-efficiency. Another aspect to point out in Figure 1 is the presence of three "sub-dimensions" that appear from the combination of the three main dimensions. These sub-dimensions are more complex to be analyzed in the sustainability framework because they integrate concepts and notions of change.

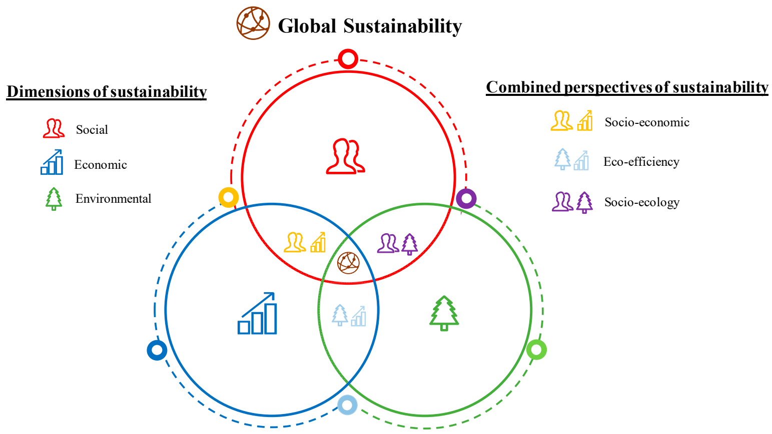

Figure 1. Dimensions of sustainability in a Venn diagram.

The sustainability assessment can be described as a progressive analysis where the evaluation complexity increases according to the analysis level. Any system (e.g., chemical process, biorefinery, productive chain) can be evaluated considering only one dimension of sustainability (i.e., economic, environmental, or social). Thus, this type of analysis is known as 1D analysis. In these analyses, the main purpose is to define if the system is feasible considering one perspective. For instance, economic assessments of different biorefinery systems have been published considering either economic or environmental dimensions. Besides, if two sustainability dimensions are involved (e.g., economic and environmental), the analysis is known as a 2D analysis. The social dimension of sustainability has not been widely included in biorefinery or chemical process analysis due to low objective indicators. Therefore, the most studied dimensions of the sustainability assessment have been the other two. Thus, 3D analysis is not typical in the open literature [7].

The economic and environmental dimensions have been the most analyzed sustainability dimensions because several indicators and evaluation methodologies are available in the open literature. Palmeros Parada et al., [7] reported a high tendency to evaluate economic and environmental sustainability dimensions. Then, the tendency is guided to publish papers only considering economic and environmental aspects. Finally, other sustainability dimensions have been included to describe the sustainability concept. Bautista et al., perform a sustainability assessment of the Colombian context's biodiesel production process [48]. For this, the authors defined five dimensions to evaluate the sustainability of the process. These dimensions were economic, environmental, social, political, and technological. Horlings discusses the cultural and personal dimensions as part of the framework to define global sustainability [65]. Thus, the sustainability concept can be complemented through the inclusion of "new" dimensions. Nevertheless, a framework ought to be defined prior includes any other dimension. According to the way to assess the sustainability, Solarte-Toro et al., [11] have divided the sustainability assessment into two ways (i) Life cycle Sustainability Assessment (LCSA) and (ii) Dimensions assessment. The first option involves the life cycle thinking concept in all the sustainability dimensions, while the second aspect does not involve it. In contrast, the dimensional assessment is conducted based on indicators and metrics published elsewhere. Both approaches difficult the comparison of the different processes analyzed. Thus, efforts should be conducted to improve this aspect. Table 2 presents different studies reported in the open literature related to the sustainability assessment of biorefineries.

Table 2. Biorefinery definitions given in the open literature.

Raw Material	Products	Process	Simulation Tool	Approach	Sustainability Dimensions			Refs.
					Economic	**Environmental**	**Social**	
Biomass	Biohydrogen	Biomass gasification	Aspen Plus	LSCA = LCA + LCC + SLCA	(Value per kg H_2) LCoH: 3.59 $€_{2017}$	(Values per kg H_2) GWP: 0.18 kg CO_2 eq. AP: 1.45×10^{-2} kg SO_2 eq.	(Values in mrh/kg H_2) GWG: 0.594 HE: 0.128	[62]
Spent coffee grounds (SCGs)	Biodiesel	Transesterification process of the extracted oil	GaBi 8.7 software	Dimensional analysis	N.R.	(Values per 1 t of SCGs) * Climate change: -0.04×100 kg CO_2 eq. FE: 5.51×0.01 kg P eq. PED: 1.26×10 GJ PM: 0.97 kg $PM_{2.5}$ eq. HTc: 0.50×10 kg 1,4-DB eq.	N.R.	[66]
Lignocellulosic residues and cheese whey and tequila vinasses	Bioethanol	Bioethanol production in a pretreatment-saccharification-fermentation train	SuperPro Designer v8.5 (SPD 8.5)	Dimensional analysis	Y: 3.07 $MJ_{out}/kg_{polysacharides}$ PC: 1.40×10^{-1} USD/MJ_{out}	(Values per MJ_{out}) Emitted GHG: 4.26×10^2 g CO_2 eq. Water consumption: 16.00×10^{-1} $L_{FreshWater}$	N.R.	[67]
Pig slurry	Heat and electricity	Anaerobic digestion	N.R.	LCA	N.R.	CC: 6.0 g CO_2 eq./MJ	N.R.	[68]
Corn straw	Hydrogen	Hydrogen production with methane tri-reforming	Aspen Plus v8.8	Dimensional analysis and LCA	TCI: 171 million USD PC: 582,216 USD PBP: 4.72 year	(Values per 1004.5 kg H_2) EC: 117,674 MJ Emitted GHG: 5409.9 kg CO_2 eq.	N.R.	[69]
Rice and coconut residues	Electricity	Biomass gasification	N.R.	LCA	N.R.	(Values per 1 kWh of electricity produced) * GWP: -13.15×10 g CO_2 eq. PM: -290.20×10^{-1} CFC-11 eq. HTP: 72.90×10 g 1.4-DB eq.	N.R.	[70]
Eucalyptus logging residues	Electricity	Biomass combustion	N.R.	LCSA = SLCA	N.R.	N.R.	(Values in mrh/1 kWh electricity) CL: 2.59×10^{-3} GWG: 1.17×10^{-2} HE: 4.22×10^{-2} FFL: 1.58×10^{-4} WSLF: 3.21×10^{-2}	[71]
Sweet sorghum	Bioethanol	Bioethanol production in a pretreatment-saccharification-fermentation train	N.R.	Dimensional analysis	PC: 735.76 USD/ha Total expense: 407.19 USD/ha	N.R.	N.R.	[72]
Avocado seeds and peels	Syngas	Anaerobic digestion	Aspen Plus v.9.0	LSCA = LCA + LCC + SLCA	PBP: 6.24 year TR: 0.81	(Values per syngas) CF: 8.99 kg CO_2 eq. WF: 6.66 m^3	M/L: 0.72 Max M/L: 0.95	[11]
Coffee cut stems	Bioethanol, electricity, and steam	Bioethanol production in a pretreatment-saccharification-fermentation train	Aspen Plus v9.0	LCA	N.R.	CC: 0.0784 kg $CO_2/MJ_{ethanol}$	N.R.	[63]

Table 2. *Cont.*

Raw Material	Products	Process	Simulation Tool	Approach	Sustainability Dimensions			Refs.
					Economic	Environmental	Social	
Rice husk	Torrefied rice husk pellets (TRH)	Partially oxidative torrefaction of biomass	N.R.	LCA	ACC: 2.32 million USD AOP: 3.14 million USD	(Values per TRH) Annual GHG emissions: 604 ton CO_2 eq.	N.R.	[73]
Wet poultry litter (WPL)	Biofuel and biochar	Gasification	N.R.	LCA	POC: 155 USD/ton CHP: 68 USD/ton	(Values per 1000 kg WPL) * HH: -6.10×10^{-5} pts EQ: -5.02×10^{-6} pts CC: 8.61×10^{-5} pts	N.R.	[74]
Waste cooking oil	Biodiesel	Transesterification process of the extracted oil	N.R.	LCA	N.R.	(Values per 1 ton produced biodiesel/day) GWP: 2.72×10 kg CO_2 eq. HTP: 2.07 kg 1,4-DB eq. FWAE: 2.86×10^{-1} kg 1,4-DB eq. TE: 1.75×10^{-2} kg 1,4-DB eq.	N.R.	[59]
Forestry residues	Heat and electricity	Biomass gasification	N.R.	TEA and LCA	Electricity cost: 0.469 USD/kWh	Emitted GHG: 91 g CO_2/kWh	N.R.	[75]
Coffee cut stems	Heat and hydrogen	Biomass gasification	Aspen Plus v9.0	LSCA = LCA + LCC + SLCA	Total cost: 15.97 million USD.	CC: 0.320 kg CO_2 eq. HTP: 0.019 kg 1,4-DB eq. PMF: 4.89×10^{-4} kg PM_{10} eq. ALO: 0.022 kg oil eq.	56 h/week 48 h/week	[76]
Paddy straw	Bioethanol	Bioethanol production in a pretreatment-saccharification-fermentation train	N.R.	LCSA = SLCA	N.R.	N.R.	Employment: 1.94 FTE/10^6 yuan Wage: 1.78 yuan/yuan	[77]
Corn stover and Lignin-rich stream	Biofuel	Hydrothermal liquefaction (HTL) + aqueous phase reforming (APR)	Microsoft Excel	TEA and LCA	MSP: 1.23 €/kg (LRS) 1.27 €/kg (CS)	GWP: 56.1 and 58.4 g CO_2 eq/MJ biofuel of Corn Stover and Lignin	N.R.	[78,79]

N.R.: No reported; LCSA: Life Cycle Sustainability Assessment; LCA: Life Cycle Assessment; LCC: Life Cycle Costing; SLCA: Social Life Cycle Assessment; LCoH: Levelised cost of hydrogen; GWP: Global Warming; CED: Cumulative Energy Demand; Mrh: Medium risk hours; CL: Child Labor; GWG: Gender Wage Gap; HE: Health Expenditure; FE: Freshwater eutrophication; PED: Primary energy demand; PM: Fine particulate matter formation; HTc: Human toxicity, cancer; Y: Yield; PC: Production Cost; GHG: Greenhouse gas; POC: Plant operation cost; CHP: Combined heat and power-generating station; HH: Human health; pts: Point for environmental impact; EQ: Ecosystem quality; CC: Climate change; ACC: Additional capital cost; AOP: Annual operating cost; HTP: Human toxicity potential; FWAE: Fresh water aquatic ecotoxicity; TE: Terrestrial ecotoxicity; EC: Energy consumption; TCI: Total capital investment; FTE: Full-time equivalent; FFL: Frequency of forced labor; WSLF: Women in the sectoral labor force; ALO: Agricultural land occupation; PBP: Payback period; TR: Turnover ratio; CF: Carbon footprint; WF: Water footprint; M/L: Minimum-to-Living wage ratio; Max M/L: Maximum Minimum-to-living wage ratio. MSP: Minimum Selling Price.
* Negative values correspond to better performance compared with a reference case.

4. Trends for Improving Biorefinery Sustainability

Improving biorefinery sustainability is linked to several activities (i) research and development of new pathways for biomass upgrading, (ii) waste streams valorization for decreasing environmental impact, (iii) finding new ways to use several feedstocks for producing different products without affecting quality and process standardization. These items are discussed below:

4.1. Waste Streams Valorization

Waste streams will be always produced in a biorefinery since not all feedstocks can be produced into valuable products. Fossil fuel use is necessary to supply the energy demand of most biorefineries systems since a logical and gradual energy transition is performed in the next years. Thus, current research studies should be addressed to minimize waste streams for decreasing the environmental impact. Liquid, solids, and gaseous streams are produced as wastes in different processes. Then, technological innovations must be proposed based on the physical and chemical state of the residues. Moreover, different value chains produced a large amount of residues, which can be upgraded by applying the biorefinery concept [80,81]. In this way, the following subsections discuss the possible upgrading of carbon dioxide and stillage as part of the most representative residues produced in biomass upgrading systems.

4.1.1. Carbon Dioxide Storage and Upgrading

Carbon dioxide (CO_2) is the most important greenhouse gas in the atmosphere, causing climate change [82]. The industrial sector contributes more than 40% of worldwide CO_2 emissions. Strategies are being implemented to manage, store, and upgrade this gas into value-added products [83]. Within the reasonable CO_2 sources that are likely to be used for the proposed upgrading alternatives, the emissions from the manufacturing and energy industry sectors have been proposed as the most suitable options. In contrast, the emissions that are produced from activities such as transportation, deforestation, livestock, or anthropogenic activities cannot be considered logical sources of this gas to be destined for value-added products. CO_2 emissions and carbon footprints of industrial processes must be decreased. Several researchers have analyzed CO_2 as a raw material in different transformation routes [83–85]. To achieve this proposal, new processing facilities (greenfield processes) or processes (brownfield processes) should be added to existing plants for upgrading CO_2 streams and producing value-added products.

Biorefineries are systems with the potential to produce CO_2 after utility production. Indeed, these processes require fuels for producing steam and directly usable energy (i.e., electricity). Thus, biorefineries are also a potential source of CO_2. In this regard, biorefinery sustainability can be improved even more if this gas is upgraded to other products while minimizing emissions. Storage and upgrading CO_2 can help to increase processes sustainability. However, low energy efficiency, unstable selectivity, and adverse catalytic stability are challenges to be overcome before the commercialization of CO_2 conversion technologies [86]. According to Kongpanna et al. [85], CO_2 is not a reactive gas. Thus, chemical processes proposed using this gas as a reactant must increase the driving force. High-value-added products can be produced using CO_2 as the source. Nevertheless, thermodynamic analysis is required to establish feasible production pathways.

Currently, the methods for decreasing the CO_2 environmental effect can be divided into two major groups (i) produce less CO_2 and (ii) avoid CO_2 emission into the atmosphere. The industrial sector is implementing strategies related to increasing the energy efficiency of power plants and combustion processes. On the other hand, the Carbon Capture and Storage (CCS) alternative has been proposed for avoiding CO_2 emissions. CCS systems can be divided into four different technologies (i) pre-combustion, (ii) post-combustion, (iii) oxyfuel, and (iv) chemical looping. Nevertheless, these processes have a high capital expenditure and a relatively low TRL [87]. For this reason, the Carbon Capture and Utilization (CCU) technology has been proposed since this scheme was proposed to upgrade

CO_2 into a valuable portfolio of products such as chemicals and fuels [87]. This trend can increase process sustainability because the social (low pollution), economic (more incomes), and environmental (low emissions) dimensions are favored. Figure 2 presents the sequence of the raw material flow from its storage to the final environmental assessment. These steps must be considered for analyzing whether the models proposed in the valorization of CO_2 allow evidencing a favorable behavior in the sustainability dimensions.

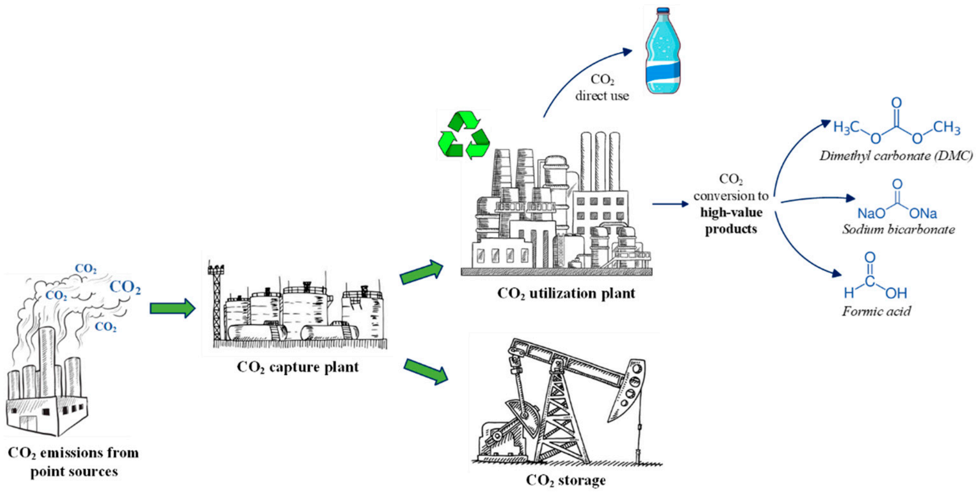

Figure 2. Flow diagram of the CO_2 capture and upgrading.

The Carbon Capture and Storage (CCS) systems use both physical and chemical absorption methods based on amines (monoethanolamine, diethanolamine, and methyl diethanolamine). The majority of CO_2 separation techniques have been based on these options. Chemical CO_2 absorption methods utilizing amine solutions are burdened by high energy requirements, large absorption columns due to poor CO_2 loading capacity, and solvent degradation by other flue gas components such as SO_2, NO_2, HCl, and O_2 [86]. Therefore, amine scrubbing is probably the only technology for Post-Combustion Capture (PCC) for CO_2 that is available to be implemented in existing plants. Li et al. [88] have reported monoethanolamine as the most commonly used amine. Nevertheless, new solvents should be researched for removing CO_2 from exhaust streams since monoethanolamine and dimethanolamine are solvents with a high environmental impact. Therefore, new ways for improving CCS systems must be researched.

CO_2 conversion processes involve the production of (i) dimethyl carbonate (DMC), (ii) sodium bicarbonate, (iii) acetic acid, (iv) formic acid, and (v) diphenyl carbonate [83]. These processes are more guided to chemical pathways using a solid catalyst. Metal-based catalysts have been the most used pathways to transform gases into chemicals at the industrial level. Nevertheless, optimization in the operating conditions and catalyst poisoning are key aspects to be improved for the full implementation of these processes. On the other hand, microbial processes also have been researched for upgrading CO2-containing streams. Indeed, products such as (i) butanol, (iii) 2, 3-butanediol, (iii) acetates, and (iv) butyrates. Several microorganisms such as *Clostridium ljungdahlii*, *Clostridium autoethanogenum*, and *Moorella thermoacetica* have been researched as potential microorganisms for producing chemicals in submerged fermentations [89]. For instance, Jack et al. observed that fermentations with H_2/CO ratios higher than 1.5 ultimately consumed CO_2 as a carbon source until reaching a final concentration lower than the initial [90]. In contrast, these authors observed that fermentations with H_2/CO ratios lower than 1.5 produce CO_2 Products such as ethanol and 2, 3-butanediol can be produced using these microorganisms while consuming CO_2. Nevertheless, higher titers are obtained at H_2/CO ratios of 0.5 [90]. Thus, more research is needed to improve this process for both CO_2 upgrading and solvent production. In this way, CO_2 can be seen as another feedstock to be considered when designing biorefineries since involving new products based on CO_2 upgrading can increase the economic performance of the process and lead to evolving current biorefineries through the integration of waste stream valorization.

4.1.2. Stillage Upgrading

The distillery industry is responsible for more than 95% of the ethanol production in the world. This organic chemical compound can be obtained from first and second-generation raw materials [91]. However, the stillage flow rate is greater than the produced ethanol. Besides, high nitrogen and organic compounds concentration in this byproduct reflects a treatment need instead of direct disposal into the environment [92]. Different strategies are being proposed for the valorization of this residue for bioenergy production to fulfill the bioeconomy principles.

The high content of organic matter, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in distillery stillage indicate a high biological activity. However, some compounds such as polyphenols, are responsible for limiting microbial degradation processes [93]. This high organic content of stillage allows for proposing several pathways for upgrading and recovery of some value. Anaerobic digestion is the most common alternative to decrease the organic load of distillery stillage. This process is suitable since the microorganism consortia can degrade several compounds. Indeed, 1 m^3 of distillery stillage could generate 38 m^3 of biogas. Even so, the pH of the stillage must be corrected to avoid problems and acidification.

The amount of carbon and nitrogen based compounds in stillage determines the biogas and methane production. For instance, Rajagopal et al. [94] concluded that high levels of ammonium (NH^{4+}) contribute to instability and low production rates of the biofuel. As for the remaining sludge, this can be destined as manure and the effluent should be treated before disposal [95]. Zielińska et al. [91] have reported different technologies for the anaerobic digestion of distillery stillage within which the anaerobic fluidized bed bioreactor (AFBR) affords the greatest yield of both biogas and methane (15.8 L/L·d and 160 L_{CH4}/d, respectively) with the shortest hydraulic retention time (HTR = 3.5 days) when compared to the anaerobic continuous stirred tank reactor (CSTR) and the anaerobic baffled reactor (ABR). When operating with high organic loading rate (OLR) and short HTR, the use of zeolites is suitable for the AFBR [96]. Therefore, anaerobic digestion processes and biogas utilization can be profiled as a potential option to decrease the energy demand of distilleries and biorefineries producing bioethanol. Biogas utilization (after moisture and H_2S removal) can decrease the use of fossil fuels (e.g., natural gas).

Distillery stillage must be pretreated before upgrading through anaerobic digestion. Siles et al. [97] stated that when using ozonation, methane production can significantly increase while the COD removal remained the same. Biogas and methane yields can be determined by recalcitrant compounds that include polyphenols and melanoidins as these represent toxicity agents for the microorganisms [95]. Different studies have established that the inhabitation occurs for polyphenol concentrations above 1 g/L. Besides, factors such as polarity, type, and molecular size also contribute to the product yield [98].

Second-generation ethanol can be obtained using distillery stillage due to the high content of polysaccharides. Before the biological transformation of this byproduct, fermentable monosaccharides are obtained by the depolymerization of hemicellulose and cellulose [99]. However, 2-furfural and 5-hydroxymethylfurfural can inhibit ethanol production as these compounds can even stop the fermentation process of the hydrolyzed ingredients. Dilute acid pretreatment can be carried out in optimal conditions for wheat distillery stillage using 0.2 M H_2SO_4 for a period of 60 min and 131 °C [100]. Enzymatic hydrolysis can be implemented to release glucose; however, furfural, acetate, and lactate constitute inhibitors during the ethanol fermentation process [101]. This alternative seems to not be promising since high operating expenditures are required. Nevertheless, stillage can be used from producing dehydrated products from the sugar content in these waste streams. Indeed, levulinic acid, formic acid, and furan-based compounds can be produced in acidic conditions. These compounds have a higher value than biofuels. These products can increase the sustainability of a stillage producing process. Yields and productivities of levulinic acid production and furan-based compounds have not been widely reported in the open literature. Thus, this is a research area worthy of research and study.

Another option for upgrading stillage is biohydrogen. This energy vector is a promising alternative for the upgrading of distillery stillage as CO_2 is not emitted [102]. This process can be carried out by using both autotrophic and heterotrophic bacteria. The latter includes dark fermentation which does not require light energy and several substrates can be used for fuel production [91]. Mishra et al. [103] studied the use of acidogenic mixed consortia (AMC) for obtaining biohydrogen from distillery stillage achieving a yield of 9.17 mol/kg_{COD}. Nevertheless, this option should be studied considering techno-economic and environmental aspects for ensuring sustainability and proper implementation.

Distillery stillage upgrading has been studied for producing biomethane, biohydrogen, and second-generation bioethanol. These processes constitute an alternative to decreasing environmental impacts as a result of the disposal of the high amount of stillage. Other alternatives such as bioelectrochemical technologies allow wastewater treatment for bioenergy production but there are still modifications to be implemented for the process improvement. Moreover, other research efforts must be conducted to increase the product portfolio derived from stillage.

4.2. Multifeedstocks Biorefineries

Multifeedstock biorefineries have been researched as a potential option to upgrade biorefinery sustainability since these facilities guarantee a constant flow of raw materials leaving aside seasonality, availability, and logistic issues. However, the implementation of these biorefineries did not have the expected feasibility results. Thus, a fixed strategy for the proper design of these systems must be defined [23,104]. The strategy can be based on an improved conceptual design [28]. Furthermore, the strategy should be able to overcome the challenges related to the low homogeneity of biomass, since efforts are required in the implementation of various pretreatment, recovery, and processing technologies for these specificities of raw materials [37]. Finally, economic, social and environmental analyses are mandatory to assess sustainability. Without these analyses, the viability of biorefineries with multiple raw materials will only indicate technical characteristics that may fail when trying to be implemented on an industrial scale.

From a technical point of view, this type of biorefinery in which various raw materials are integrated is more complex than traditional ones and even oil refineries. However, the effort to develop designs for these processes has been advanced because the benefits of these processes are considered. When raw materials are integrated into a biorefinery, it is possible to maximize the value generated by using the fractions of the components of the heterogeneous raw material. Additionally, several costs within the process are reduced such as the costs associated with duplicating the equipment (if raw materials are taken independently) and, in turn, reduces energy costs and helps the demand for energy in a more efficient way than a single raw material biorefinery [23].

Another important aspect related to multiple raw material biorefineries is that it minimizes the effects that price changes can generate from them. This aspect is key for developing small-scale processes since the economic feasibility of a process with multiple raw materials is not highly affected by the price change. Thus, multifeedstock biorefineries can be used as a potential strategy for boosting rural bioeconomies in developing countries where large amounts of biomass are not valorized [23]. If there are biorefineries based on a single raw material, fluctuations in the price or even in the acquisition of the raw material will force the owners of the process to redesign it, reduce scales, and may even stop production, such as the case of a company in the United States where they obtained biodiesel during the years 2005 to 2008 [105]. These problems can be solved and avoided with the biorefineries of multiple raw materials since it is possible to find relationships of those raw materials that allow them to buffer the changes that occur in the process due to the change in prices. Besides, the biorefinery will depend on all the raw materials together and this means that within its design, a versatile range of operations is considered, which allows defining different integration relationships of raw materials [106]. Even though the different benefits generated by the development of these biorefineries are recognized, the obstacles continue to feel challenging, such as the challenge related to achieving maximum efficiencies in the processes through the integration of the biorefinery platforms, which is related to the composition of feedstocks [107].

4.3. New Ways for Biomass Upgrading

4.3.1. Bioactive Compounds

The extraction of bioactive compounds such as terpenes or phenols has become an essential process when considering a biorefinery. The main reasons for this trend are the high costs of these compounds in the market and the increased demand in the pharmaceutical and food industries. A new perspective is the biotransformation of these compounds to cause structural changes. The application of terpenes is defined depending on the configuration they present. Enantiomeric terpenes have different organoleptic properties [108]. The compounds obtained are still considered natural. The mixture obtained from biotransformation has higher antimicrobial and repellent properties [109]. In terpenes, biotransformation allows for obtaining stereoselective compounds [110]. A wide variety of studies have been published in which enzymes, cell extracts, whole cells of bacteria, cyanobacteria, yeasts, microalgae, fungi, and plants are used to carry out this process [111]. Of these, the most studied biocatalysts are bacteria and fungi. An example is the fungal lipoxygenases used for the oxidative transformation of the terpenes in citrus essential oils, the bioconversion of limonene into cis/transcarveol, carvone and the biotransformation of citronellal into p-menthane-3,8-diol yields products [112].

4.3.2. Proteins

Most applications are addressed to upgrade cellulose, hemicellulose, starch, and oily components. First, second and third generation raw materials produce solid wastes rich inorganic salts and nitrogen compounds (e.g., proteins and peptides) [113]. These nitrogenous compounds have received special attention recently because these components can be used as valuable ingredients for food and feed applications. Sar et al. reported the production of protein-rich fungal biomass from potato protein liquor [114]. The separation of proteins and peptides should be conducted before other processes since nitrogen-based compounds are susceptible to pH and temperature changes. The extraction of proteins and peptides can improve the economic performance of the biorefinery because these compounds have a high value in the market [115]. On the other hand, proteins can be used for producing free amino acids, which can be used as a valuable source of chemicals (e.g., packaging materials) [116].

4.3.3. Lignin

One of the main components of lignocellulosic biomass (15–25% w/w) is lignin, the second-most prevalent terrestrial biopolymer. By using various extraction techniques, this hetero-polymer can be separated from agricultural waste, specialty crops, or wood [113]. A complex aromatic macromolecule called lignin comprises three different phenyl propane monomers (p-coumaryl, coniferyl, and sinapyl alcohols). It is difficult for bacteria to degrade these components because numerous different forms of stable chemical connections cross-link them [117]. Lignin can be used to produce several products, such as phenolic compounds and phenolic acids. Lignin can be upgraded via thermochemical processes, chemical processes, and biological processes. Lignin has been used as a binder for pellet making, creating materials, and producing high value added compounds [118].

4.3.4. Catalysis Involving

Catalysis is present in almost all chemical processes since most chemical reactions occur at special conditions for high yield and selectivity [119]. Heterogeneous and homogeneous catalysis has been involved in biomass upgrading processes in different stages, such as pretreatment and reactions [120]. Nevertheless, heterogeneous catalysis has been researched since the possible catalyst recovery and re-use. These advantages decrease the environmental impact of different processes while increasing efficiency and conversion. For this reason, heterogeneous catalysis has been researched and implemented in thermochemical processes (i.e., gasification, combustion, hydrothermal liquefaction) and biotechnological processes (i.e., biocatalysis). Indeed, several papers have reported the advantages and disadvantages of heterogeneous catalysis [121,122]. One of the most important advantages of heterogeneous catalysis over homogeneous catalysis is related to easy separation and recovery. This advantage can help to improve the economy of the process. Even so, more efforts to overcome issues such as poisoning, stability, and cost should be reviewed. The most important drawback of heterogeneous catalysis is related to the use of noble metal catalysts, which can produce a high environmental impact. This kind of metal catalyst has been used in thermochemical processes [123]. Lignocellulosic biomass conversion involving a catalytic process can contribute to reaching faster energy transition, and fossil fuels independence goals. Several reviews describe catalytic pathways for biomass upgrading into biofuels and platform molecules [124,125]. Nevertheless, a deep overview of the effects of implementing catalytic processes in biorefinery sustainability should be analyzed. Furthermore, biomass to biofuels based on catalytic processes is one of the most researched issues today. Thus, this topic will represent a great improvement in future biorefineries.

5. Potential Implications of Biorefineries: The Orange Peel Waste Case

In citrus agro-industries, 50% of the fruit is considered a residue called Orange Peel Waste (OPW). The current disposal of the OPW is in sanitary landfills generating economic and environmental problems. Some OPW recovery alternatives are the extraction of essential oil, pectin, compost production and animal feed. However, the economic viability of these alternatives is limited by low production yields, the inefficient use of biomass and lack of socio-economic and cultural contextualization of the valorization routes. In the open literature, various configurations of OPW biorefineries have been proposed from the technical, economic, environmental and social dimensions. Ortiz-Sanchez et al., [126] analyzed different OPW biorefinery scenarios to be implemented in a small orange juice production factory that generates 140 kg/h of waste from the mechanical extrusion of the fruit. Currently, OPWs are disposed of in the local landfill generating transportation costs and large amounts of leached greenhouse gases. Figure 3 presents the different biorefinery scenarios analyzed.

The biorefineries were analyzed considering three approaches of complexity (low, medium and high) from the inclusion of processing units and use of each OPW fraction (i.e., essential oil, pectin, bioactive compounds, cellulose, hemicellulose, lignin and protein). The biorefinery scenarios were evaluated from the technical dimension based on experimental data, and economics considering the Colombian and environmental context from a cradle-to-gate approach. In this sense, the technical dimension was carried out from the calculation of mass and energy initiators of the biorefinery scenarios from experimental data. The economic dimension determined the economic pre-feasibility of the biorefineries based on indicators such as the Net Present Value (NPV) and the period of return on investment. Finally, the environmental dimension was analyzed from the stage of cultivation of the fruit to the current disposal in sanitary landfills and the recovery alternatives. The OPW biorefinery scenarios were:

(i) Stand-alone process: pectin production by acid hydrolysis.
(ii) Low complexity biorefinery: extraction of essential oil by steam distillation and biogas by anaerobic digestion.
(iii) Medium complexity biorefinery: extraction of essential oil, extraction of bioactive compounds (i.e., hesperidin) with supercritical fluids, pectin extraction and biogas production.

(iv) Highest complexity biorefinery: extraction of essential oil, extraction of bioactive compounds, pectin extraction, production of fermentable sugars from the enzymatic hydrolysis of cellulose and biogas production.
(v) Highest complexity biorefinery: extraction of essential oil, extraction of bioactive compounds, pectin extraction, acetone butanol and ethanol production from the fermentation of fermentable sugars and biogas production.

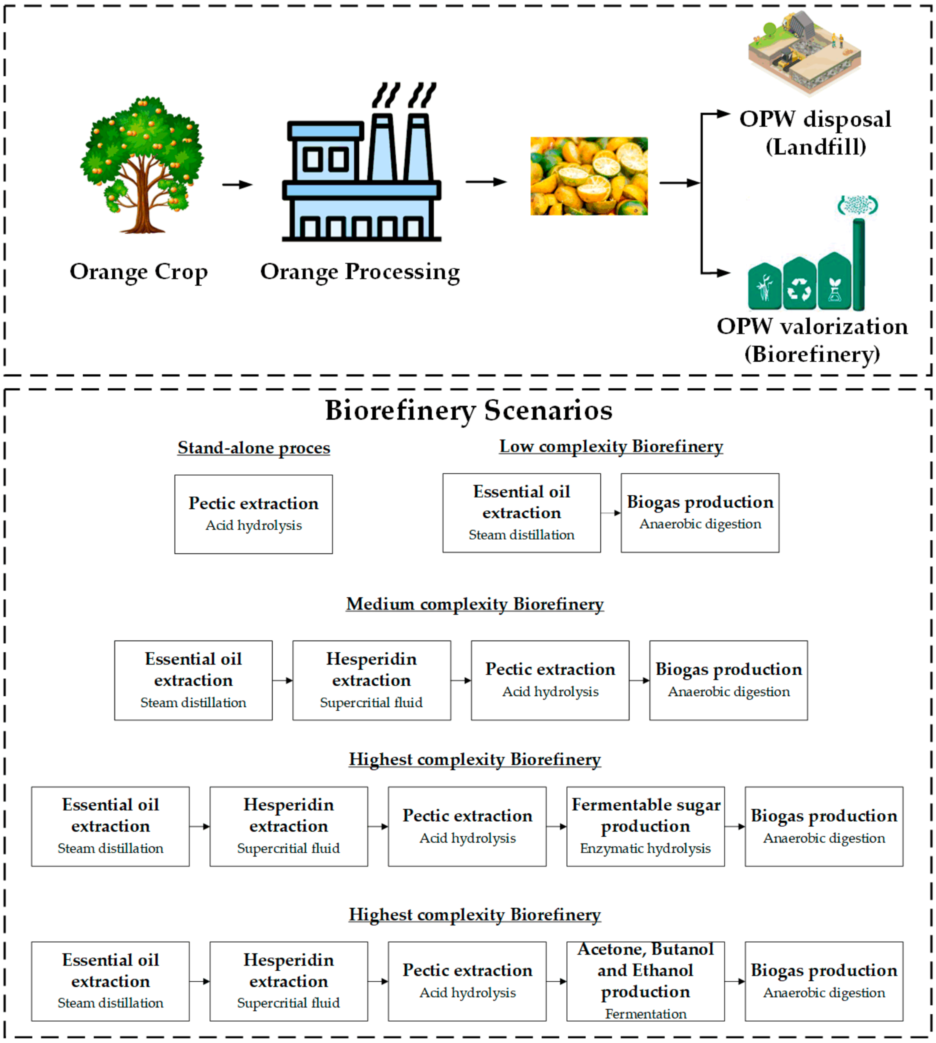

Figure 3. Orange Peel Waste Valorization applying the biorefinery concept.

The analysis of the technical dimension was analyzed considering the processing units separately. In this sense, the extraction of essential oil and biogas are those with the lowest consumption of raw materials and energy. On the other hand, the extraction of bioactive compounds and pectin are the processes that present the highest consumption of raw materials (i.e., carbon dioxide, and ethanol, among others). The pectin extraction process is the one with the highest profit consumption. This is due to the stage of recovery and recycling of the ethanol used for the precipitation of the extracted pectin. In the case of the extraction of bioactive compounds, energy consumption is significant due to the carbon dioxide pressurization stages. In addition, it is necessary to use refrigerants to maintain the conditions in the supercritical state of carbon dioxide. The production of fermentable sugars presents low consumption of raw materials and energy.

The analysis of the economic dimension gave the result that none of the biorefineries are viable at the scale analyzed. However, the authors performed the economic analysis by varying the scale of processing, resulting in the biorefinery with the highest pre-feasibility being the one with low complexity (i.e., extraction of essential oil and biogas) at a scale greater than 82.65 ton/day. On the other hand, the standalone process for the production of pectin was the scenario with the lowest economic pre-feasibility due to the high operating costs. The second scenario that presented economic viability at higher scales was the highly complex one that involves the production of acetone, butanol and ethanol. This is due to the sales costs of hesperidin (bioactive compound) and butanol.

Finally, the analysis of the environmental dimension showed that in the cultivation stage, obtaining 1 kg of orange has a carbon footprint of 1.42 kg COe eq. The agronomic activities that have the greatest social impact are the addition of agrochemicals such as fertilizers, herbicides, and insecticides, and the consumption of diesel by the machinery used and the transportation of inputs. Other impact categories that are reflected in the environmental analysis were terrestrial acidification and human toxicity. The environmental analysis of the disposal of the OPW in sanitary landfills was 6.4 kg CO_2 eq. For the biorefinery scenarios, the environmental impact was 3.5 times lower than the disposal of OPWs in landfills.

The case study allows us to elucidate the potential of different biorefinery configurations to improve the economic profitability and environmental performance of an existing plant. This study demonstrated the advantages provided by the biorefinery concept in real existing plant facilities. Specifically, pectin extraction is not the best option to upgrade OPW. In contrast, essential oil and biogas production were the best alternatives since the capital expenditure is not too high.

6. Conclusions

Biorefineries play an important role in reducing the environmental impact caused by the excessive use of fossil fuels. These facilities are evolving constantly since new developments have been appearing as a result of the research of new pathways for upgrading biomass. Carbon dioxide storage and upgrading, stillage valorization, multifeedstock use, and new products proposal based on recent trends is the base for increasing biorefinery sustainability. Nevertheless, this concept requires a standardized way to measuring and comparing this metric with other biorefineries or designed processes. This aspect is key to obtaining reliable and feasible results. The case study allowed us to demonstrate the influence of biorefinery implementation on the economic and environmental performance of a biorefinery in the agroindustry.

This review can contribute to knowing some of the most important challenges and perspectives to increase biorefinery sustainability. Indeed, this review paper highlights waste stream minimization, new pathways for upgrading biomass, and multifeedstocks use as the most important issues for improving biorefinery design. Moreover, this paper provides some examples related to carbon dioxide storage and upgrading, as well as stillage use as a potential source of valuable chemicals. Several research ideas can be extracted from this manuscript (e.g., levulinic acid production from stillage, energy matrix diversification by introducing several renewable energy sources in a biorefinery system, and analysis of rural bioeconomical development by introducing modular biorefineries). Finally, this review paper offers to the readers much updated information about the most recent trends, challenges, and perspectives. This information can be used as the basis for proposing novel biorefinery designs based on the context and recent developments.

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