Sustainable design of biorefinery processes: existing practices and new methodology

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Abstract: Nowadays, eco-designing products is increasingly practiced. The next challenge for sustain-ability is to optimize production processes. Biorefi neries are particularly concerned with this improve-ment, because they use renewable resources. To identify the contribution of transformation processes to the overall environmental impacts, Life Cycle Assessment (LCA) appears as the adequate method. A literature review highlights that LCA is mainly performed on biorefi neries to compare biomass feed-stocks between them and to a fossil reference. Another part of environmental LCA compares the impacts of different processing routes. Nevertheless, these evaluations concern already designed pro-cesses. Generally, processes are considered as a unique operation in assessments. However, some criteria like operating can notably modify environmental burdens. The eco-design of biorefi nery pro-cesses can be guided by coupling process simulation to LCA. This method has been emerging in the chemical sector in recent years. Consequently, this paper proposes a new methodological approach to assessing the complete sustainability of biorefi nery processes, since its fi rst design stages. In addi-tion to coupling process simulation and environmental LCA, the other pillars of sustainability will be assessed. Indeed, Life Cycle Costing and Social Life Cycle Assessment can be performed to obtain an integrated methodological framework. The simultaneous optimization of the environmental, economic, and social performances of the process can lead to antagonist ways of improving. Consequently, compromises should be realized. Thereby, the multi-objective optimization can be accomplished by a metaheuristic method supported by a decision-making tool. Finally, the main limits of this method and some perspectives and ways for improving are discussed.

Keywords: Life Cycle Assessment; eco-design; sustainability; modeling; process simulation; biorefi nery; biomass; multi-objective optimization; decision-making process

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Introduction

Since the beginning of the Industrial Revolution, worldwide development and the global economy have been based on the use of fossil resources, mainly petroleum, coal, and natural gas. For the first time in the modern history of human society, this growth is threatened. Actually, the current way of development brings out two major issues: the depletion of fossil reserves and the constant increase of environmental damages. Consequently, one of the most important challenges is to establish the future of the global industry, which has to be based on the use of renewable resources, having a long-term vision and respecting the requirements of sustainability.

In 1987, a definition of sustainable development was proposed by the World Commission on Environment and Development (WECD): sustainable development is a development that meets the needs of the present without compromising the ability of future generations to meet their own needs. [1] Basically, making a system more sustainable is to make it progress simultaneously on three dimensions: economy, social, and environment.[2]

To fight against the degradation of the environment, Life Cycle Assessment (LCA) seems to be the most powerful tool.[3] Indeed, sustainable development and LCA are closely linked.[4,5] Moreover, biorefineries appear as the most logical substitute of petroleum-based refineries. Indeed, this emerging concept permits to develop a wide range of bio-based products, such as chemicals, fuels, base molecules for other applications, etc. Moreover, biorefineries could be implemented everywhere, and plenty of current industries could be transformed into biorefineries, as pulp and paper plants for instance[6] or sugar can industries.[7] However, the assessment of the environmental performances of these biorefining activities is crucial, to justify the expected benefits of such operations contrary to classical production routes.

This paper presents for the first time the biorefinery concept and the environmental LCA methodology. This section also highlights the interest of using LCA to assess biorefineries. Secondly, a state-of-the-art environmental LCA of biorefinery processes is detailed. This literature review offers the opportunity to identify improvement opportunities, and so on to propose a new methodology to perform Life Cycle Sustainability Assessments (LCSA) of high-detailed biorefining processes. This methodology is based on coupling process simulation and LCA. The three dimensions of sustainable development are assessed, and a multi-objective optimization is performed. Finally, some of the future main challenges and limits of this new methodological framework are explored.

Assessing biorefinery processes with LCA: a necessity

Biorefinery concept

Nowadays, there is an urgent necessity to develop alternatives to fossil resources-based industry.[8] These non-renewable materials not only provide energy, but also a wide variety of organic chemicals. Biomass appears like the most promising option to cover these applications.[9,10] The term biomass designates renewable organic matter, like trees, agricultural crops, algae, and various residues or wastes.

The emerging concept of industries able to create a large range of products from renewable resources is called biorefining. [11] This term puts in evidence the important similarities with petroleum refineries. Indeed, multiple products can be generated from a biomass feedstock, which lead to maximize the utilization of raw materials. This analogy is represented in Fig. 1.

The working field of biorefinery systems started its development since the beginning of the 1990s. The biorefinery concept was defined for the first time in 1997: green biorefineries represent complex (to fully integrated) systems of sustainable, environment and resource-friendly technologies for the comprehensive (holistic) utilization and the exploitation of biological raw materials in the form of green and residue biomass from a targeted sustainable regional land utilization.[12] A biorefinery can also

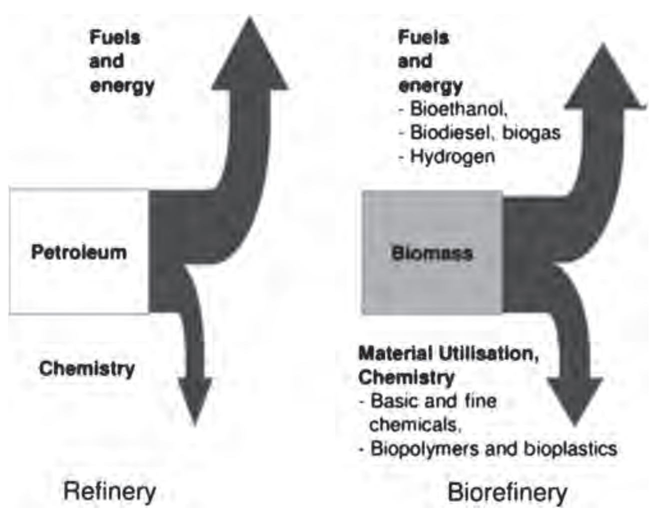

Figure 1. Analogy between petroleum refining and biorefining principles, from Kamm B. et Kamm M.[12]

be defined as sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, and chemicals) and energy (fuels, power, and heat). [13] The American National Renewable Energy Laboratory (NREL) published the definition: '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 bio-based industry.'[14]

Depending on the type of raw materials used to produce biofuels[15] and bio-based products,[16,17] biorefineries can be classified into three generations. Therefore, first-generation biorefineries are based on the direct use of traditional forms of agricultural biomass, such as corn, maize, sugarcane, or soybean. Second-generation types use lignocellulosic feedstock, mainly composed of cellulose, hemicellulose, and lignin. Finally, industrial facilities which use agricultural residues, forestry, petroleum, and urban waste, or microalgae as feedstock biomass constitute the third generation.[18,19] In some publications, a fourth generation is described: the 'biorefinery two-platform concept', where biomass is treated simultaneously by a sugar and a syngas platform.[20]

Currently, first-generation biorefineries are the most developed around the world, and particularly in the USA, Canada, and Brazil. Nevertheless, this type of biorefinery is increasingly contested, for two main reasons: change of land use and competition with food production. As a consequence, there is a growing interest for lignocellulosic feedstock, which is low-priced and abundant.[21] Second-generation biorefineries are mainly installed in the USA, China, and Canada. Nevertheless, there is a growing interest from Northern Europe countries. Microalgae biorefineries are presently at a research and development stage. Nevertheless, some third-generation biorefineries based on the use of waste (animal, food, and urban wastes) already exist in Europe. Another potential advantage of the development of biorefineries is the availability of local raw materials. This point could be essential to avoid environmental impacts caused by transportation, and could stabilize the rural economy, which will be a major step toward sustainability.[22,23]

Moreover, the choice of raw materials to use is crucial, because it involves the choice of final developed products. Indeed, biomass types can have strong composition differences, and in this way lead to create different products.[24] Figure 2 offers a representation of the paramount potential of final products which can be developed in a biorefinery.

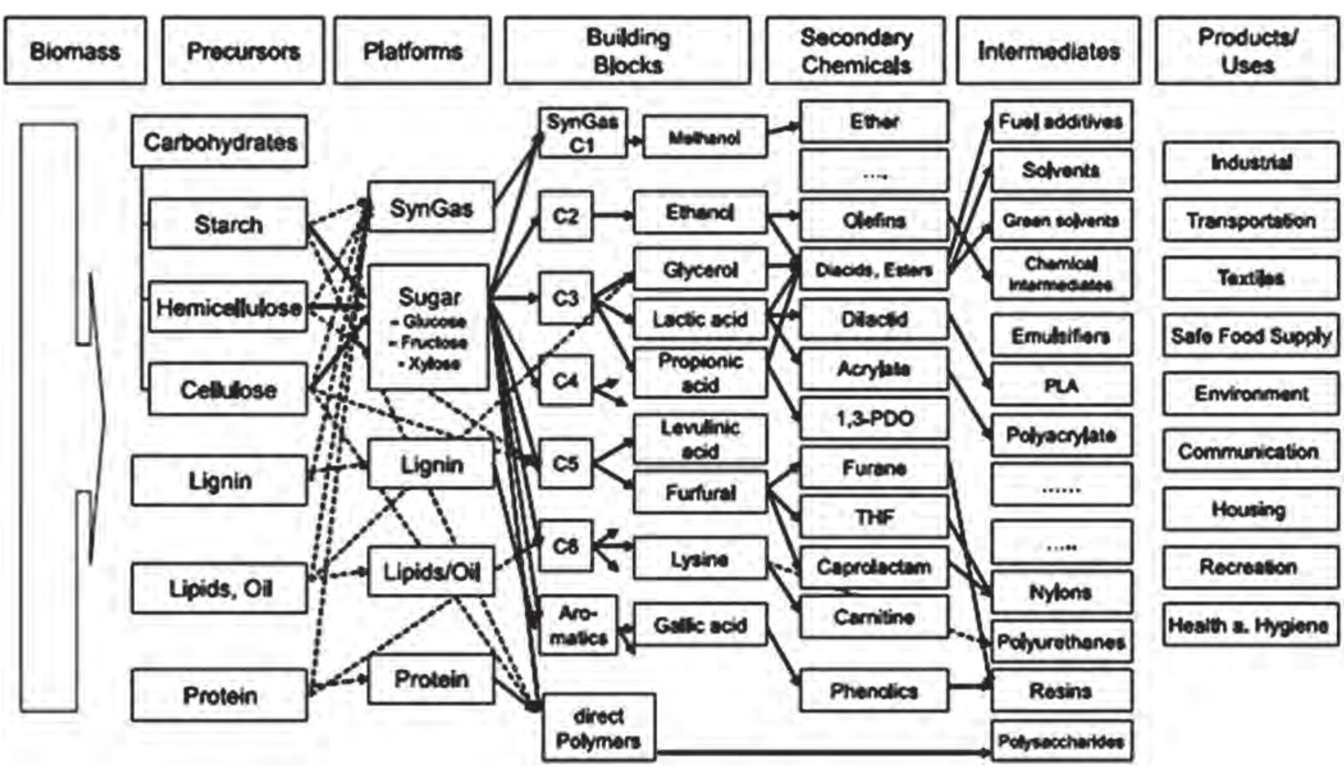

Figure 2. Simplified model of a bio-based product flow-chart for biomass feedstock.[17,20]

To execute the transformation of the biomass, following different steps, biorefineries are constituted of physical, chemical, biological, and thermal processes.[9,18,20,25–27] This wide variety of production processes is a necessity to transform biomass feedstock mixes, because the composition of these renewable resources can strongly vary from one sort to another.[28] Literature largely describes the biorefinery production processes. For instance, a detailed list of the different separation processes which can be found in a biorefinery has been developed by Huang *et al*.[29] Moreover, biorefining involves an optimization of production processes, in order to make the most efficient use of feedstocks and to maximize the economic situation of the facility.[30]

Life Cycle Assessment (LCA) methodology

LCA, as defined by the Society of Environmental Toxicology and Chemistry (SETAC), is 'a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and material uses and releases to the environment; and to identify and evaluate opportunities to effect environmental improvements'.[31,32]

A detailed report of the chronological evolution of LCA since its beginning in the 1970s, and the future challenges have been performed by Guinée *et al.*[33] Initially, LAC was only practiced on products, but the methodology can also be applied to a process or a service, and to all sectors such as the automotive industry, agriculture, chemical industry, construction, etc. LCA of industrial processes can be used to choose the best solution during the design stage.[34,35]

The LCA methodological framework, normalized by two international standards (ISO 14040 and ISO 14044),[36,37] proposes to achieve LCA by completing four different steps:

- Goal and scope definition: This step defines the objectives and the field of the study, the function of the system, the functional unit, and the limits of the system.
- Inventory analysis: This phase collects and quantifies all inputs of the studied system (renewable and non-renewable raw materials and energy) and outputs (emissions in air, water, and soil) on the whole product life cycle. Several methods to perform the life cycle inventory compilation can be found in the literature. [38]
- Impact assessment: This stage groups inputs and outputs to determine their relative contribution to environmental burdens and damages. This step is certainly the most complex, and a wide variety of impact assessment methods have been developed: ILCD 2011,[39] IMPACT 2002+,[40] ReCiPe 2008,[41] etc. The impact assessment can be realized at midpoint or endpoint levels.[42]
- Interpretation: Practitioners can identify improvement opportunities for the studied system. Moreover, a sensitivity analysis can be performed on the results of the LCA to identify the parameters or variables that have the strongest influence on environmental impacts. Knowledge of highly sensitive data or settings will guide the search for technical solutions to reduce environmental loads of the studied product.[43]

Nowadays, the LCA community constantly expands, and there is a crucial need to work with robust methods and tools. With this objective, international or European working groups are more and more developed, such as the International Reference Life Cycle Data System (ILCD) which publish series of handbooks,[39] or the European Life Cycle Database, a completely free database to generalize and grant a large access to LCA. Finnveden *et al.*[44] proposed a synthesis of crucial developments in LCA, such as database development, methods enhancement, etc.

Interests of performing LCA on biorefinery processes

The will of biorefinery industrials to use biomass feedstock to practice an environmentally friendly manufacturing system is laudable, and a decisive step for the future. Nevertheless, producing more sustainable outputs can be complex and replacing fossils by renewable and green resources is not sufficient to enable the transition to a clean and sustainable industry. Indeed, a particular attention is crucial on several points such as the choice of biomass feedstock or transformation processes.[9] As a matter of fact, creating a product from biomass could require more energy or reagents than the fossil-based equivalent.[45] The importance of incorporating environmental considerations to Process System Engineering (PSE) field, traditionally focused on economic and technical constraints, is emphasized in perspective works since the beginning of the twenty-first century,[46–48] and some environmental or socials burdens are systematically assessed during the design phases of a process. For instance, health and safety issues and the control of emissions from the plant are generally taken into account.[49] Nevertheless, plenty of crucial impacts are still neglected (acidification, eutrophication, etc.). Environment problematic is currently considered as a non-priority and their improvements are considered when the process is operating.

However, to avoid potential pollution transfers from a life cycle phase to another, a life cycle approach is essential to assess the production processes. Using the LCA method appears like the most promising method, because it permits to consider the life cycle of the process itself, closely linked to the product life cycle, as illustrated in Fig. 3. Indeed, the life cycle of a process starts with research and development stage, followed by design and construction steps. The operational phase comes after. This is generally the most understood and assessed step. Finally, the end-of-life of a process is generally composed of disassembly, decommission, and restoration steps.[48,50,51] Consequently, performing an environmental LCA leads to an expansion of the boundaries of the assessed system, by taking into account upstream and downstream processes [52,53] and not only consider the operational phase.

LCA of biorefineries: literature review of existing practices

Commonly, process design only considers technical and economic criteria in most sectors, to guarantee the feasibility of a product and to maximize profit. These considerations are essential for biorefineries, too. However, environmental criteria, assessed by environmental LCA are crucial and need to be integrated to the design of modern plants [54] and particularly of biorefineries. A significant number of LCAs applied to biorefining facilities can be found in the literature. In this paper, these studies are separated into two main groups: LCA of biorefinery inputs (raw materials) and products and LCA of biorefinery processes. The first group of studies generally takes into account the impacts on the environment of plant activities, but they are considered as a unique operation, without distinguishing and separating the different processes parts encountered in the biorefinery (pre-treatments, extractions, separations, purifications, and others). The second group focus on studies which offer a higher detail level, and permit to have a better understanding of the operational phases.

Environmental LCA for biomass feedstock choice

Even more than for other industrial sectors, the inclusion of upstream activities is essential for biorefineries. Indeed, transformation processes used in the plant can operate with a large amount of different biomass feedstocks. Consequently, the choice of raw materials is a crucial step in the environmental analysis of a biorefinery. In this way, a large part of environmental LCAs of biorefineries are focused on differences on environmental impacts induced by the choice of the biomass feedstock. For instance, Jeswani *et al.* [55] drive a comparative LCA of lignocellulosic biorefineries which produce bioethanol using four different inputs: wheat straw, poplar, Miscanthus, and forest residue. This study also compare these scenarios to ethanol production from fossil resources. As expected, they highlighted important reductions on eight environmental impacts among 12 assessed by using biomasses instead of fossil resources. Moreover, significant variations exist

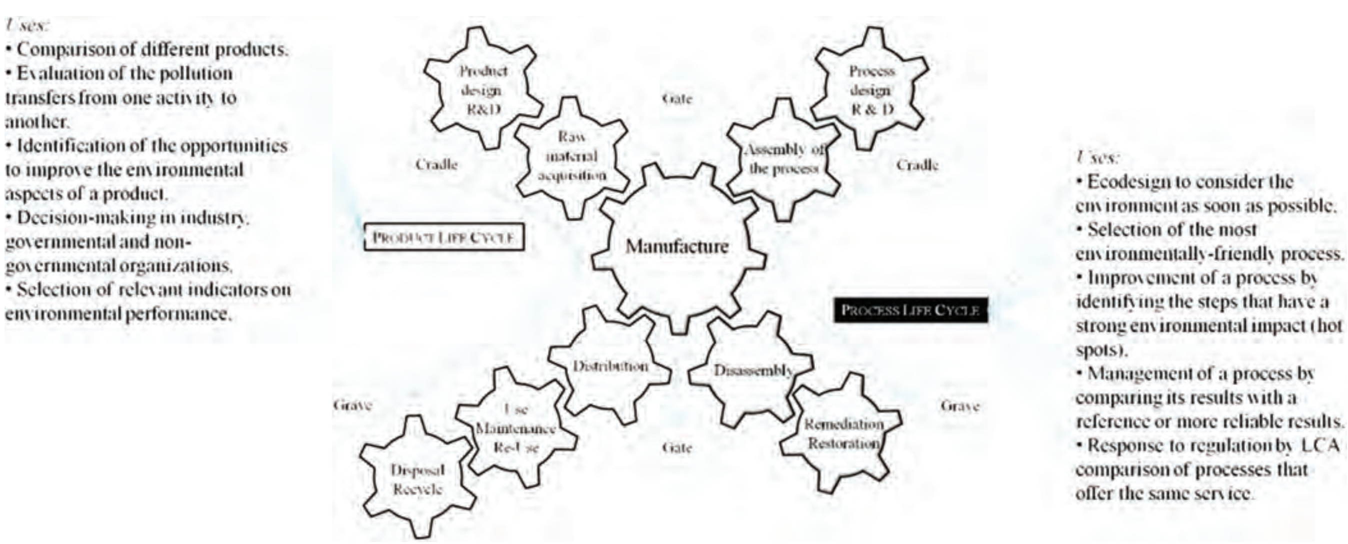

Figure 3. Links between product and process life cycles, from Jacquemin *et al*.[51].

between renewable feedstocks too. Indeed, ethanol from forest residue appears like the most promising option, and ethanol from wheat straw as the worst, mainly due to the important burdens generated by land use change. Undeniably, land use change effects are a crucial point.[56] The paper clearly explains that each option offers reduced environmental impacts concerning greenhouse gas (GHG) emissions compared to fossil resources. Nevertheless, the paper puts in evidence that forest conversion to Miscanthus cultures leads to a raise of GHG emissions, because the sequestration potential of Miscanthus is less important than forests sequestration potential. In contrast, the conversion of grassland to poplar growth drives to additional GHG savings. Cherubini *et al.*[56] also achieved an assessment of a biorefinery based on switchgrass to produce ethanol, energy, and chemicals. This LCA compares results to a fossil reference system. In this case, too, a biorefinery facility offers better performance than the classic refinery, with gains on GHG emissions notably. Nevertheless, two impacts are superior in the biorefinery scenario: acidification and eutrophication. In the same way, Mu *et al.* [57] compared the environmental impacts in these cases, for different raw materials (wood chips, corn stover, waste paper, and wheat straw). Nevertheless, the assessment is focused on only three impacts: GHG emissions, water consumption and energy use, which are generally the main issues for industry. Several studies highlight the potential environmental benefits of second generation biofuels compared to first generation biofuels. For instance, Mu *et al.* [58] assessed the environmental burdens (energy consumption and GHG emissions) of a palm-oil-based biorefinery. Third-generation biorefineries, based on the use of algal biomass, are still not very developed. However, they have a strong potential, because the cultivation of this biomass could bring to a more efficient way to capture CO_2 emissions. Cherubini *et al.* [59] performed an LCA of a bioethanol biorefinery based on wood, but considered only GHG emissions and energy consumption. Nonetheless, this paper shows the potential of biorefineries. Indeed, this system could reduce GHG emissions by 40% and non-renewable energy savings by 84% in 2050. In addition, Uihlein and Schebek[60] performed comparative LCAs between variants of lignocellulosic biorefineries and a fossil refinery. This study exposes the significant advantages of a biorefinery compared to a classic way: a reduction of 40% of total environmental impacts for the production of lignin, ethanol and xylite instead of acrylic binder, gasoline, and sugar.

Consequently, the review of these papers highlights the importance of assessing and comparing feedstocks by LCA. Indeed, this approach permits identification of the potential benefits of using biomass instead of fossil resources. Nevertheless, it also puts in evidence the strong disparity between the different types of biomasses, some of whose cultures can lead to additional environmental burdens (eutrophication and acidification for first-generation biomass feedstocks cultures notably). However, a focus on biomass feedstock is not enough. Indeed, Singh *et al.*[61] proposed a review of LCA of algal biofuels. This study puts in evidence the importance of understanding and assessing the process operations too. Indeed, some key issues such as the necessity of recycling the water used for harvests, or the significant energy consumption of several unit operations such as drying and hexane extraction are identified.

Comparative LCA of alternative processing routes

Another part of LCA of biorefineries explore alternative processing routes. For example, Jeswani *et al.*[55] experimented with the comparison between thermochemical and biochemical conversions of biomass to ethanol. This assessment points the advantages of using a thermochemical route instead of a biochemical process to produce ethanol from poplar and forest residue. The comparison between these two alternative processing routes can be found in other publications, such as Mu *et al.*[57] Moreover, Cherubini *et al.*[62] practiced an evaluation of corn stover and wheat straw conversion by thermochemical and biochemical treatments. Furthermore, Gilani *et al.*[63] practiced a consequential LCA of five different processing routes for the extraction of hemicelluloses, and Kenthorai Raman *et al.*[64] assessed three different catalytic processes for biodiesel production. In both cases, different scenarios were modeled, as classic LCA, and then compared to identify the best solution.

Uihlein *et al.*[60] experimented with a different way to assess the environmental performance of a biorefinery, in an eco-design and optimization objective. Indeed, they assessed six different scenarios which represent possible variants for the processing route of the future biorefinery. These alternatives consider the possibility of adding acid or heat recoveries, or using lignin to provide heat or electricity. These assessments reveal the main hotspots, i.e., the most contributing activities to environmental impacts. So, three processes generate the major part of environmental impacts: provision of straw (80% on carcinogenics, 88% on land occupation), acid (65% on total impact score), and heat (20% of total climate change). Furthermore, comparison between the different scenarios highlight the potential gains. Finally, this LCA also underlines potential improvements thanks to the establishment of recovery systems for acid and heat: with respective recovery rates of 95% and 80%, an additional reduction of the impacts appears, from 30% to 90% depending on assessed categories compared to the base case biorefinery. In the same way, Jacquemin *et al.*[65] assessed the environmental impacts of a part of a biorefining process. Indeed, they determined water consumption and carbon dioxide emissions generated by the ultrafiltration step of an extraction and purification process of arabinoxylans. This study highlighted the paramount contribution of operating conditions to environmental impacts. Modahl *et al.*[66] accomplished an LCA of a timber and woodchips based biorefinery, which produce six different products. They avoided the allocation procedure by modeling processes at a detailed level. Consequently, they could identify the most contributive processing steps. Borrion *et al.*[67] reviewed the different environmental LCAs of bioethanol from lignocellulosic biorefineries. Finally, Brentner *et al.*[68] carried out one of the most complete LCAs applied to biomass conversion processes. Indeed, the aim was to identify the most encouraging pathways to implement an environmentally responsible plant destined to produce biodiesel from algal biomass. For this purpose, the biorefining system is separated into five processing stages: cultivation, harvesting, lipid extraction, conversion, and disposal or reuse. Moreover, different technologies are considered for each step. Consequently, there are 160 different combinations, i.e., possible paths. This cradle-to-gate study aims to identify the best design option. To simulate the plant, models are used, such as algae growth parameters, bioreactor design, harvesting, extraction and end-of-life of residue. The best promising global route is determined by assembling each unit process consuming less energy, by a single objective optimization. In a second time, a comparative LCA between the currently practiced scenario and the optimized route is achieved. Results put in evidence a global improvement of the environmental performance thanks to the establishment of the less energy consuming alternative. Indeed, the second scenario induces a reduction of 86% of greenhouse gases emissions. Moreover, water use is reduced by 48%, and land area requisitioned by 58%.

To conclude, in most cases, production processes are not modeled in LCAs. They are considered as black boxes, i.e., a global and irremovable operation. Generally, there is a unique operation, named 'biorefinery plant', [56] which groups all engaged processes, such as pre-treatment, hydrolysis, fermentation, combustion, etc. Nevertheless, their complexity is well above it. Plant operations are a succession of unit operations (UO), which all have inputs and outputs. All these blocks are linked, and operate with synergy: a change on a unit operation will involve changes on the linked unit operations.[48] Currently, scientific publications related to environmental LCAs does not completely highlight the specific contribution of each unit operation to environmental damages, despite the fact that it may lead to better optimizations of process chains. [69] This practice begins to emerge on some application fields: water treatment, chemical industry[70,71] or metallurgy[72] for instance. Jacquemin *et al.* [51] proposed a review of LCA applied to processes in various sectors; nevertheless it is still not applied to biorefineries.

Coupling LCA to process simulation tools

In this way, a preliminary LCA achieved at the first design steps could permit identification of the main potential hotspots, and then to have a particular attention to these critical points.[73] Moreover, the sustainability of a biorefining facility is actively related to an efficient use of raw materials and to an optimal mix and arrangement of processes. A biorefining process sequence can be considered as a complex organization of physical, chemical, biochemical, or thermochemical processes. In this way, it is essential to identify the most promising alternative. [9] This challenge can be performed by coupling LCA to process simulation tools like ProSimPlus®, Aspen®, Chemcad®, or SuperPro® for instance. Indeed, simulating the complete sequence of a process could allow a more detailed comprehension of industrial activities of a product life cycle. Undeniably, this innovative approach offers the opportunity to understand the impact on the environment of a process, at the scale of unit operations, and to assess the contribution of operating conditions on environmental burdens. Indeed, two variables are generally the most influent on the economic, technical and environmental performances of a process: structure and operating variables.[74]

Coupling process flow-sheeting and LCA is an emerging practice. The aim is to simulate a process sequence to obtain mass and energy balances, which can after be used as data for the life cycle inventory step.[75] It could be useful to avoid the recurrent issue of collecting complete and reliable data, for LCA realization. Azapagic *et al.*[49] proposed a methodological framework based on these principles. Indeed, they detailed guidelines to realize Process Design for Sustainability (PDfS). The first step is the project launch. During this step, it is crucial to identify all the assessed criteria, the possible alternatives, and the main stakeholders. Then, the preliminary design phase can start. Process simulation is accomplished, to obtain mass and energy balances. Then an LCA is practiced. In parallel, an economic evaluation is realized to evaluate the feasibility of the alternative. Finally, a detailed design step can be performed, with a full assessment of sustainability. Azapagic *et al.*[54] practiced this methodological framework to a vinyl chloride monomer plant. Chemical industry had a pioneering role in the development of this methodology, probably encouraged by high stakes and reliable process simulation software. Indeed, Alexander *et al.*[76] applied this new methodology to a nitric acid plant. They used Hysys® tool to model the facility, and to obtain mass and energy balance information. Then, an LCA and an economic analysis (based on capital and operating costs) are performed. A multi-objective optimization determines the most promising options and eventual trade-offs. Guillén *et al.*[77] assessed the hydrodealkylation (HDA) of toluene process, with the aim of minimizing costs and environmental impacts. This same process has also been optimized by Ouattara *et al.*[78,79] with the minimization of costs and of five environmental burdens. Furthermore, Fermeglia *et al.*[80] developed a similar method by using PROII® or Aspen® and applied it to chemical industry (maleic anhydride production process). A similar approach has been practiced on milk concentration processes.[81] Finally, Mery *et al.*[82] experiment the link between process simulation software and LCA to water-treatment processes. This assessment underlines the influence of unit operations and of operation conditions changes. A global tool has been developed by using Python programming language and the LCA software Umberto® as a basis.

The link between Process System Engineering and environmental LCA is increasingly practiced in the chemical sector, as explained by Jacquemin *et al.*[51] which compared 18 major research works on this field. This approach also emerges in the biorefining area, but its application is more complex, due to difficulties encountered to characterize solid biomass in software developed for chemistry. Wang *et al.*[83] experimented the search of an optimal and sustainable design of a biorefinery based on a gasification pathway. For this study, they performed a multi-objective optimization. The objectives are based on two aspects of sustainable development: economy and environment. Indeed, the aim of this application is to determine the optimal configuration to minimize the environmental impact and to maximize the economic viability of the company. The economic objective is represented by the net present value (NPV), and the environmental goal by the minimization of global warming potential (GWP). To perform this work, Wang *et al.*[83] created a superstructure which includes a wide range of models for several alternative functional blocks, for each step of the global process. GWP is calculated by a gate-to-gate LCA. The multi-objective optimization allows the evaluation of the best technologies for each unit operation, the most advantageous operating conditions, all the ideal flow rates, and the equipment sizes to maximize NPV and to minimize GWP. Jeswani *et al.*[55] practiced a comparative LCA of conceptual designs of a biorefinery producing bioethanol. To accomplish this study, they implemented gasification models developed by the NREL in Aspen Plus®. They modeled four different biorefineries, depending on the dedicated feedstocks: wheat straw, forest residue, poplar, and Miscanthus. The comparison of the environmental profiles of the four biorefining options put in evidence the high potential of the ethanol production by thermochemical route applied to poplar and forest residue. Mayumi *et al.*[84] realized the assessment of a plant producing biomass-derived resins. They used Aspen Hysys® to simulate the process operations, and then realized an LCA-based on mass and energy

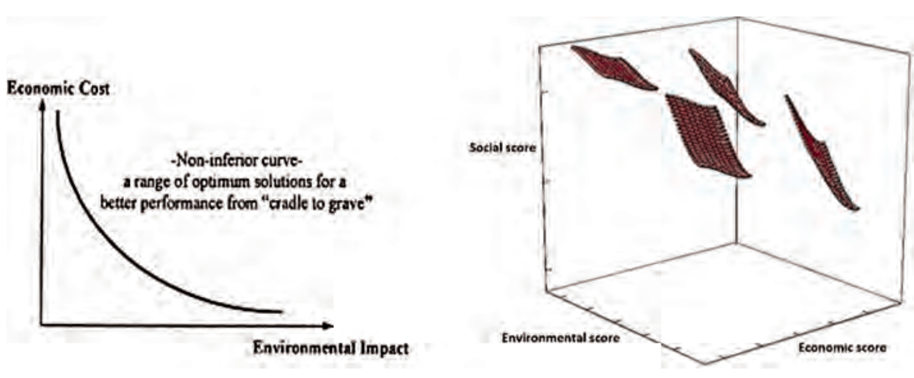

Figure 4. 2D and 3D Pareto curves obtained in multi-objective optimizations.[93]

balances obtained before. A similar approach have been used by Morales Mendoza *et al.*[85] to realize the eco-design of a bioethanol production facility, reusing waste vegetables. Indeed, this paper highlights the high interest of coupling LCA to a process simulation process. Morales Mendoza *et al.*[85] used AspenHysys® and Ariane® to respectively simulate the biodiesel production process and the energy plant. So, the life cycle inventory is based on mass and energy balances obtained from the process simulation. Moreover, a cost estimation is realized, and a multi-objective optimization puts in evidence the optimal configurations to minimize the environmental damages (on human health, ecosystem quality, climate change and resources depletion) and to maximize profit. Gerber *et al.*[86,87] also worked on the development of a superstructure to assess and improve production processes with a multi-objective optimization (minimization of global warming potential and production costs) applied to energy systems and to a Synthetic Natural Gas biorefinery.[88–90] Alvarado-Morales *et al.*[91] worked on the LCA of a bioethanol biorefinery, simulated on PROII®. So, a base case design is assessed first, followed by alternative designs. Finally, Pereira *et al.*[92] assessed a sugarcane biorefinery processes by using a process simulators to obtain mass and energy balances.

To conclude, coupling LCA and process simulation software to feed the life cycle inventory and to optimize the processing route (with the choice of unit operations and operating conditions) is an emerging and very promising method to enhance the environmental profile of industries. Increasingly practiced in the chemical sector, this approach is increasingly used for the establishment of biorefining plants. A further step seems to be the integration of the other pillars of sustainable development: social and economic considerations. Table 1 summarizes these studies.

This section highlighted the impacts of raw materials and processing routes on the environmental performance of a biorefinery. If the comparison of several biomass feedstocks is commonly performed, the high-detailed assessment of processing routes is a less-studied research topic. Commonly, the assessments of processes are performed on already in use production systems, based on plant data. This approach only allows the improvement and redesign of existing technologies. Moreover, the section put in evidence that realizing an LCA based on results of process simulation can be a powerful tool to propose an innovative solution before the process construction, and to really work on the eco-design of a process. So, it is crucial to assess environmental impacts since the beginning of a project, with technical constraints jointly, in an integrated path.[93,94] The assessment of environmental performance at each design stage would unable a better optimization of the process.[48]

A new methodology to integrate sustainability considerations to the biorefinery process eco-design

The previous section put in evidence some strong improvements in process system engineering and LCA fields. Nevertheless, it also highlighted some lacks, to achieve sustainable assessments and sustainable design of biorefinery processes. The objective of this section is to propose a new methodology to facilitate the eco-design and sustainable development of biorefinery processes, dealing with possible difficulties by assessing simultaneously the three dimensions of sustainability.

Application of multi-objective optimizations to biorefineries

Nowadays, designing more sustainable processes is one of the key challenges for the development of a more environmentally friendly industry. Nevertheless, this aim can only be reached with a synergetic integration of social, economic, and environmental criteria, through a life cycle perspective. This vision should be applied to biorefineries, because this type of industry which offer greener fuels and chemicals[19] seems to be the most promising option to transit to this more sustainable society.[95] Nevertheless, the optimization of a system on multiple objectives is complex, because criteria are generally antagonist. Moreover, categories have to be optimized in the same time, and not one after the other.

Historically, multi-objective optimization has been experimented by process system engineering practitioners in order to reduce wastes,[96,97] energy use and costs. Next, additional constraints, like technical and operability issues have been implemented. Finally, the adding of environmental impacts followed, with mitigate results. Indeed, one of the main challenges was to apply a life cycle approach to the environmental analysis, even if upstream and downstream activities cannot be governed by plant operators.[76]

Currently, the main challenge is to develop a tool which will be a help for the choice of the best processing route. Indeed, arbitrating and choosing between different scenarios can be complex. Moreover, another crucial point is to perform a multi-objective optimization of environmental, economic, technical, and social considerations

Table 1. Application fields and characteristics of studies dealing with LCA and simulation of biorefinery processes.

Source	Application field	Assessed processes	Simulation	Environmental LCA
Wang *et al*. [83]	Hydrocarbon biorefinery via gasification pathway	Drying of the cellulosic biomass feedstocks, air separation unit, gasification, syngas conditioning, Fischer–Tropsch synthesis, hydroprocessing, power generation, and the diesel and gasoline production	Equations representing each unit operation	Gate-to-gate GWP or a single metric, the total eco-indictor 99
Jeswani *et al*.[55]	Thermo-chemical biorefinery for bioethanol production	Feedstock cultivation, handling and drying, gasification, syngas cleanup and conditioning, synthesis, alcool separation	Aspen Plus®	Cradle-to-gate GWP, ADP, AP, EP, FAETP, HTP, MAETP, ODP, POCP, TETP, Land use
Mayumi *et al*. [84]	Biomass-derived resins (polyethylene and polypropylene)	Ethanol-route process and syngas-route process	Aspen Plus® and Aspen HYSYS®	Cradle-to-gate Greenhouse gases emissions
Morales Mendoza *et al*.[85]	Biodiesel Production from waste vegetable oils	Acid-catalyzed process	Aspen HYSYS® Ariane®	Cradle-to-gate Human health, ecosystem quality, climate change, resources depletion
Gerber *et al*.[86-90]	Synthetic natural gas (SNG) production process from woody biomass	Thermochemical production	-	Cradle-to-gate Ecoscarcity06, Ecoindicator99, GWP
Alvarado-Morales *et al*.[91]	Bioethanol production	Heterogeneous catalysis, enzymes, homogeneous catalysts, fermentations, purification steps	PROII®	Gate-to-gate
Pereira *et al*.[92]	Butanol production in sugarcane biorefineries	Cleaning, extraction, concentration, fermentation, distillation, dehydration	-	Cradle-to-gate ADP, AP, EP, GWP, ODP, HTP, POCP

GWP, global warming potential; ADP, abiotic depletion potential of elements and fossil fuels; AP, acidification potential; EP, eutrophication potential; FAETP, freshwater aquatic ecotoxicity potential; HTP, human toxicity potential; MAETP, marine aquatic ecotoxicity potential; ODP, ozone depletion potential; POCP, photochemical ozone creation potential; TETP, terrestrial ecotoxicity potential of a process. Some optimizations of one or two of these criteria already exist, and especially for biorefining activities. Economic and environmental optimizations are realized, such as the example of design of VCM plant,[98] or for absorption cooling systems.[99] Some assessments of the complete sustainability of plants already exist. Indeed, Santoyo-Castelazo and Azapagic[100] accomplished the optimization of energy systems, with a life-cycle approach. Seventeen criteria have been used, such as GWP, abiotic depletion, security, and diversity of supply or capital costs. Moreover, Carvalho *et al.*[101] developed a tool to assess the sustainability of different chemical process alternatives, named SustainPro®. Some economic evaluations of biorefineries are available,[66,102,103] such as a few attempts to integrate economic and social considerations into LCA.[104] Gassner *et al.*[105] practiced a multi-objective optimization of a biorefinery producing fuel by the thermochemical route. Nevertheless, this optimization is focused on thermo-economic criteria, and environmental considerations are excluded. Janssen *et al.*[106] realized a multi-objective optimization on both environmental and economic considerations, with a goal of retrofit process design, i.e. the transformation of a pulp and paper industry into a wood-based biorefinery. Another optimization of economy and environment has been practiced on a biorefinery.[107] The environmental consideration is not complete, because only the global warming potential is assessed. Nevertheless, the optimization model can improve a large variety of parameters, such as the production capacity, size of unit processes, operating conditions, flow rates, yields and materials and energy consumptions. You *et al.*[108] realized a sustainability assessment of the biofuels supply chain. The economic aspect is represented by the total annualized cost, the environmental objective by GHG emissions, and the social indicator is the number of accrued local jobs. Even if the three pillars of sustainability are assessed, it is restrictive to reduce an aspect to a unique indicator. For instance, the environmental problematic is more complex than the climate change issue only. Finally, to introduce new perspectives, a more global vision may be applied to assess the sustainability of a biorefinery. Indeed, the whole supply chain could be analyzed, and a market analysis could be performed, such Mansoornejad *et al.*[109] highlight it. Table 2 summarizes these assessments.

These assessments highlight the difficulty to perform a complete evaluation of the sustainability of a process. Indeed, only a few studies consider the three pillars of sustainable development. Besides, these dimensions have to be evaluated with a life cycle approach.

A new methodological framework for the integrated assessment of the sustainability

Figure 5 exposes a global representation of the new methodology proposed for the sustainability optimization and design of biorefinery processes. This schema highlights the importance of defining the most suitable parameters for each UO, which will lead to important changes on the three areas of sustainability. The following part describes each step of the new methodological framework in detail.

First of all, to assess the complete sustainability of processes, it is essential to determine which indicators will permit to attribute a score, a mark to the various scenarios. The best option to assess the sustainability aspects is to use life cycle oriented methods: Environmental Life Cycle Assessment, Life Cycle Costing (LCC), [18,110–112] and Social Life Cycle Assessment. [104,113] A large choice of indicators to achieve these assessments is available. [114,115] For example, economic evaluation can be based on feedstocks and products costs, on capital costs or on return on investment. Internal costs such as budget for research and development or company costs can also be used as indicators. [45] Social assessment on the other hand can be assessed with metrics such as the number of jobs, health issues, land availability, gender equality, etc. [19] Exactly like environmental LCA, social LCA, and LCC require large amount of data. Environmental LCA is fed by coupling with a process simulator, to obtain the required mass and energy balance. Generally, the data gathering is easily practicable for LCC. Nevertheless, Social LCA is an emerging methodology, still on development, and acquire information can be complex. Even if the interest of applying social LCA at the earlier design stages is obvious, this methodology is in reality often practiced at the end of the development, because more data are available. [45] So, environmental LCA, LCC, and social LCA appears like the most relevant methods. [116] An integrated methodology covering the three dimensions of sustainability can be initiated, similar to the LCSA. [45,117–119]

The next step of the proposed methodology is the realization of a multi-objective optimization. Indeed, when the assessment of the three pillars of sustainable development has been achieved, it is necessary to identify a solution to optimize the process on these three categories (environment, economy, and social). Nevertheless, the choice of the best solution is complex due to the conflicting objectives. Thereby, designing sustainable processes necessarily force engineers to make choices and agreements between the different stakeholders, [48] because optimizing many criteria simultaneously rarely brings to an ideal solution, which

Table 2. Multi-objective optimizations considering sustainability criteria.

Source	Application field	Sustainability considerations	Methodologies	Indicators
Khan *et al.*[98]	Vinyl chloride plant	Environment, economy	LCA, economic analysis	GWP, ADP, ODP, HTP, EP, AP, POCP, operating costs
Gebreslassie *et al*.[99]	Absorption cooling systems	Environment, economy	LCA, economic analysis	Eco-indicator 99 unique score, total annualized cost
Santoyo-Castelazo and Azapagic [100]	Energy systems	Environment, economy, social	LCA, LCC, social LCA	GWP, ADP, AP, EP, FAETP, HTP, MAETP, ODP, POCP, TETP, capital costs, total annualized costs, levelised costs, security and diversity of supply, public acceptability, health and safety, intergenerational issues
Carvalho *et al.*[101]	β-galactosidase production	Environment, economy	LCA, economic analysis	GWP, ODP, POCP, AP, EP, HTP, AETP, TETP, cumulative cash flow, purchase cost, utility cost
Lundberg [102]	Biorefinery	Economy	Economic analysis	Annual earnings, break even, profit opportunity
Wright and Brown[103]	Biorefinery	Economy	Economic analysis	Capital costs, operating costs, biomass costs
Gassner and Maréchal[105]	Biorefinery	Thermo-economic	-	Energy efficiency, exergy efficiency, operating costs, total production costs
Janssen *et al.*[106]	Biorefinery	Environment, economy	LCA, economic analysis	GWP, POCP, Ecotoxicity, AP, ODP, Human health non-cancer, EP, Human health cancer, Human health Particles, Profitability, Investment, Energy economics, Supply chain profit
Gebreslassie *et al.*[107]	Biorefinery	Environment, economy	LCA, economic analysis	GWP, net present value
You *et al.*[108]	Cellulosic Biofuel	Environment, economy, social	LCA, economic analysis, social input-output anaysis	Total annualized cost, greenhouse gas emissions, number of accrued local jobs
Mansoornejad *et al*.[109]	Biorefinery	Environment, economy	Market analysis, techno-economic study, LCA, supply chain analysis	-

GWP, global warming potential; ADP, abiotic depletion potential of elements and fossil fuels; AP, acidification potential; EP, eutrophication potential; FAETP, freshwater aquatic ecotoxicity potential; HTP, human toxicity potential; MAETP, marine aquatic ecotoxicity potential; ODP, ozone depletion potential; POCP, photochemical ozone creation potential; TETP, terrestrial ecotoxicity potential; AETP, aquatic ecotoxicity potential reaches maximum gains for each category. In most cases, these categories are antagonist. For instance, reduction of environmental impacts can involve a diminution of the maximal realizable profit. Consequently, it is necessary to perform a multi-objective optimization [93] to identify all the possible solutions to optimize simultaneously the three assessed dimensions (environment, economy, and social).

So, the methodology consists of determining objectives functions for each criterion which needs to be optimized.

The optimization of such complex systems generally leads to an important number of practicable solutions, represented by Pareto frontiers or surfaces. [75] Pareto fronts obtained for two-objective and three-objective optimizations are represented on Fig. 4.

The determination of these Pareto surface can be really complex, that is why a large part of studies which relate multi-objective optimization generally consider the environmental impacts as a single score, or with one burden, often climate change. Genetic algorithms can be used in order to reduce the optimizing time. [120,121] Another method is to identify indicators which vary with the same tendencies, and to find independent variables. Indeed, Azapagic *et al.* [75] optimized a boron product system, and discovered a link between different impacts, such as GWP, acidification and human toxicity. Consequently, the optimization can be realized with GWP only, and related impacts will decrease too.

The last part of the innovative methodology is the choice of a solution. For this step, it is crucial that stakeholders can understand and identify gains and losses for each solution. Indeed, it is important to understand that a multi-objective optimization permits to reach optima which are different of the ones obtained with a single objective optimization. Consequently, environmental, economic, or social best scores determined separately will be unattainable by a multi-objective optimization. To facilitate the decision-making process and to permit to stakeholders to realize trade-offs, several tools can be used. A first method consists in the attribution of different weights to each criterion, depending on its importance [18,76] to calculate the best solution. Nevertheless, this method forces stakeholders to promote criteria. To avoid it, it is possible to assign the same weight to each criterion. Another solution is to choose the alternative for which all criteria differ from their optimal values with the same percentage, as mentioned by Azapagic *et al.* for the assessment of the boron system.[75] Decision-making can also be supported by the multi-attribute value theory method (MAVT) or by the analytical hierarchy process (AHP). [122] Wang *et al.* realized a review of decision-making methods. [123] To choose between the different alternatives, it is essential for all the different stakeholders to make trade-offs, and so to base the eco-design of the process on a global understanding of the system. [74]

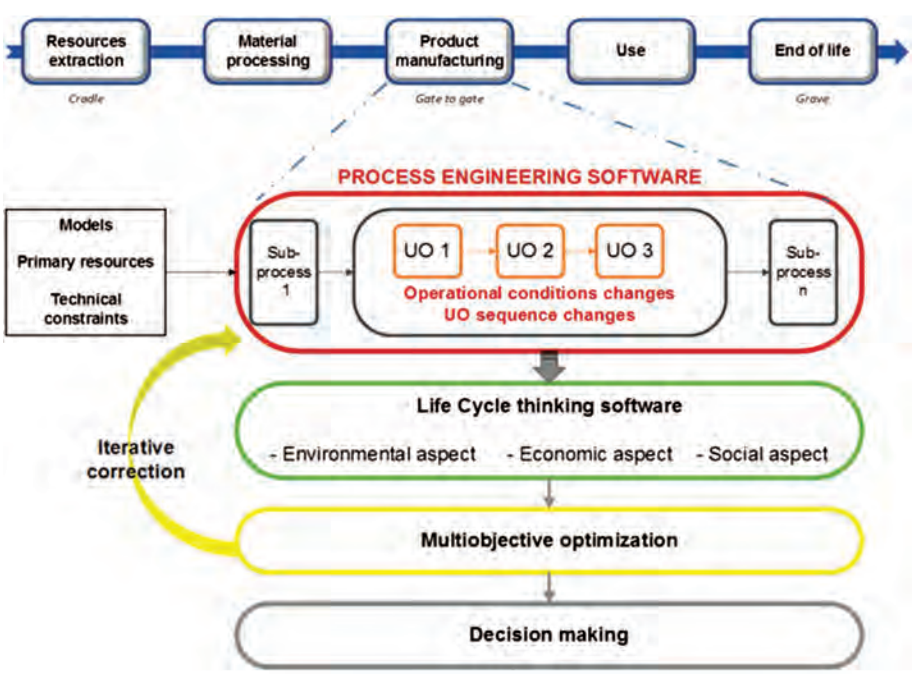

Figure 5. Methodology for Sustainable LCA coupled to process simulation software.

Challenges and future trends

The implementation of this new methodology and its associated tools is subject to several barriers. Indeed, these limits can be classified in several groups: barriers linked to the application of environmental LCA, limits related to biorefining processes simulation step, and concerns about the assessments of the other dimensions of sustainable development (social LCA and LCC). Finally, some reflections are formulated as an opening to link this new methodological framework with other environmentally friendly methods, such as green chemistry.

Limits linked to environmental LCA

Choice of the functional unit and allocation issue

Nowadays, production processes can create a large range of products or energy simultaneously. One of the main issue with the LCA of multi-products processes is the choice of an adapted functional unit (FU), and by the way, the choice of an allocation method to determine the relative contribution of each final product on the environmental burdens. [124] Assumptions are often decided, like considering one product as the main output, and all the others like co-products, wastes, or residues. However, biorefineries produce high-value goods, such as chemical compounds, which cannot be considered as wastes. [125]

To identify the most suitable FU, several methods can be tested. Cherubini *et al.* [56] based their assessment on the amount of biomass treated per year (dry matter). A similar approach is used by Uihlein *et al.* [60] who base their works on the quantity of biomass entering the biorefinery. Sometimes, assessments are realized by using various functional units.[18] The choice of an FU is easier for biorefineries producing energies exclusively. Indeed, the Renewable Energy Directive[125] bases every assessment on the same FU: 1 MJ of fuel. Nevertheless, this approach does not take into account the different types of biofuels.

Moreover, the quality of the product is an important consideration and should be specified in the functional unit. For instance, the production of a high purity cellulose at 95% will lead to different operating conditions and so on different environmental impacts than the production of 80% pure cellulose.

The choice of the allocation method is also a crucial step, because it will strongly impact the final results of the LCA,[126–129] For instance, Luo *et al.*[130] compared LCA results obtained with different allocation rules on a corn-stover-based biorefinery. In this case, a mass and energy allocation shows a reduction of global warming potential compared to classic gasoline production. Nevertheless, the economic allocation suggests opposite conclusions. The international standards ISO 14040 and ISO 14044[36,37] advise to avoid the allocation when it is possible. The best option is to increase the level of detail of the model, to separate a multifunctional process into several sub-processes. If this method is not practicable, an expansion of the system should be considered, by substitution or by enlargement.[131] To perform the LCA of a biorefinery producing ethanol, Jeswani *et al.*[55] used the system expansion approach. If it is impossible, the allocation has to be based on physical properties of products (mass or energy typically), or on other links, such as an economic allocation for example. Nevertheless, an economic allocation is not fully reliable for the assessment of biorefineries, because it is still an emerging sector, and raw materials and products prices could strongly vary. [132] Cherubini *et al.* [59] assessed bioethanol biorefinery and proposed a comparison of results depending on the allocation procedure used. Brankatschk *et al.* [133] developed a new allocation method for LCA of agricultural activities. Indeed, they based this allocation procedure on the Cereal Unit, a common denominator from Germany used to compare different agricultural products. This new method leads to intermediate results between mass/energy and economic allocations results. Ahlgren *et al.* [134] proposed a detailed paper on the allocation issues for biorefineries. To conclude, defining a universal allocation method to apply is impossible. The allocation procedure has to be chosen and can be different for each situation. [126]

Assessment of the whole life cycle

Designing a sustainable biorefinery process can be executed from three different perspectives. First of all, the choice of the biomass feedstock is essential, to ensure a constant and enduring supply and to minimize the environmental impacts related to the upstream agricultural activities. Secondly, the process performances have to be enhanced, based on consumptions and emissions linked to the process chain. Finally, a complete assessment of final products is compulsory, to determine its sustainability from environmental, economic, and social aspects.[18] Consequently, a biorefinery should be assessed with a cradle-to-grave approach, to take into account the complete life cycle, and not to neglect potentially primordial and significant activities, such as transportation to and from the installation site, cultivation steps, and final products end-of-life.[19] The agricultural sector is one of the main contributors to climate change, via important GHG emissions. Consequently, it is compulsory to take these significant impacts into account when assessing a plant linked to agricultural activities. A sustainable upstream agriculture must be organized, based on economic, environmental, and social considerations.[135] Nevertheless, a cradle-to-grave study is often difficult or even unrealizable, due to the wide range of final products and usages. Consequently, data collection on the future of products at the output of the plant is complex. In this way, the cradle-to-gate alternative is generally preferred to avoid this issue. For instance, Azapagic *et al.*[70] realized a cradle-to-gate assessment of the system processing boron ores to make five different products, to identify the key unit processes and improvement possibilities.

In the literature, cradle-to-grave assessments of pulp and paper industry can be found.[136] This kind of industry is very similar to biorefineries.[137] Indeed, pulp and paper factories can be considered as basic biorefineries, and a large part of current biorefineries are in reality former paper production plants.[9,138] Consequently, assessing a biorefinery on the whole life cycle is possible, and could permit to identify hotspots outside of the plant gates. Indeed, significant impacts are caused by transportation or by cultivation methods. Moreover, LCAs of upstream activities could be used as an argument to choose the most environmentally friendly biomass for future biorefining applications.[139] For instance, woodchips are considered as one of the most encouraging feedstocks. Nevertheless, this apparent sustainability is highly correlated to the cultivation stage. Indeed, wood can be produced by natural or artificial regeneration methods. Artificial regeneration uses fertilizers especially, and consequently generates more environmental burdens (in particular acidification and eutrophication, caused by nitrogen and phosphorous emissions). Thereby, the choice of woodchips as feedstock has to be argued, because it is not systematically the best opportunity. [140] Additionally, important divergences exist concerning the way to quantify biogenic carbon linked to crops, i.e. the carbon which is sequestrated during the plant growth.[141–146] To conclude, performing a cradle-to-grave LCA is crucial to assess a biorefinery, to avoid pollution transfers and to take into account the complexities linked to biomass feedstocks.

Attributional or consequential LCA

One of the main difficulties in the LCAs of industrial processes is the choice of the LCA type.[18] Indeed, an LCA can be attributional or consequential.[44,147] An attributional LCA is based on physical flows which are constant through the whole life cycle, whereas consequential LCA illustrates the change of flows to and from the environment, resulting from different potential decisions.[134,148] These two types of LCA generate important differences in the final results.[149] As biorefining is an emerging field, a consequential LCA could be interesting to determine effects of the market on the future of biorefineries. Nevertheless, a comparison with an attributional LCA, which is well-established and reliable, will be necessary to avoid aberrant results.

Land-use change issues

The section *Limits link to process simulation* highlighted the interest in assessing a biorefinery on the whole life cycle, and not only with a gate-to-gate approach. Indeed, a cultivation step is essential for biorefineries. Nevertheless, harvesting biomass feedstocks for industries may lead to additional impacts. A major issue is land-use changes. Indeed, the increasingly important demand for biomass in biorefineries induces the development of feedstock cultivation for first-generation biofuels mainly. However, this intensive farming causes several issues. First of all, land availability is not infinite and the continuous growth of the biofuels plant field imposes a partition of land and water between biorefineries feedstocks and food sector.[55] Moreover, intensive agriculture could decrease the soil quality and then affect production yields on a long-term approach. Finally, land-use changes can lead to a significant increase in GHG emissions. Indeed, even if the carbon sequestration effect occurs (biogenic carbon captured by the crop during its growth), additional GHG emissions can be caused. For instance, Azapagic[19] assessed the GHG emissions for different feedstocks. Thereby, a land conversion to harvest Miscanthus for ethanol production in the United Kingdom generates 3.6 times more GHG emissions than petroleum-based ethanol production. Moreover, the carbon sequestration in soils has to be assessed with a long-term vision. Indeed, C is captured into three different spheres: soil, vegetation, and wastes. A land-use change disturbs this equilibrium, which needs 20 years to be re-formed. During the first 20 years following a land-use change, there is an important gain on GHG emissions due to the CO_2 sequestration in soils. Nevertheless, after 20 years, the land attains an equilibrium and cannot capture CO_2 anymore. [56] Moreover, some cultures generate a reduction of GHG emissions, like switchgrass, but others can induce a significant increase of emissions.

To conclude, the development of second-generation biorefineries is essential, because land-use change issues could be avoided by the replacement of dedicated crops by woody biomass and wastes from agriculture or forestry activities. Furthermore, the effects of land-use change should be assessed systematically,[134] with an appropriate indicator, like GHG benefit per unit of land.[56] Moreover, a major use of existing local renewable resources should be applied as often as possible. Indeed, this approach could permit minimization of the environmental burdens caused by raw materials transportation.[150] The benefits of local supply of biomass are well-known, especially for the pulp and paper industrial sector.[151]

Other environmental impacts uncertainties

One of the major benefits of LCA is to avoid focusing on a unique impact (generally climate change), to assess a wide range of impacts simultaneously. This particularity applied to biorefineries highlights the quasi-systematic increase of two environmental impacts: eutrophication and acidification. [60] Fertilizers based on nitrogen and used for crop cultivation appear to be the main cause of this phenomenon. [56] Another paramount damage caused by the installation of biorefineries is a loss of biodiversity. Indeed, this phenomenon can appear, induced by land transformation and a standardization of harvested crops. Nevertheless, the opposite effect can also be detected, by transforming degraded lands into cultivated fields. This change could lead to an increase of biodiversity. [19] To go further, the water demand can be a significant and crucial issue when a biorefinery is developed. Indeed, water consumption is strongly correlated to the nature of the harvested biomass. [19] Consequently, special attention is required for this indicator. Moreover, a distinction should be made between water streams and water quality. Indeed, a comparison of the quality of input and output water of a process could be a powerful indicator. Finally, there are strong uncertainties concerning the N_2O emissions mainly caused by using fertilizers. Indeed, the Intergovernmental Panel on Climate Change (IPPC) guidelines advise to consider that 1.325% of N from a fertilizer is emitted as N in N_2O. However, recent works suggest the use of higher factors, between 3 and 5%. [56,152] Considering the significant impacts associated with synthetic fertilizers, such a paramount uncertainty is a major issue. To conclude, it is essential to keep the paramount advantage of the environmental LCA: the multicriteria assessment. Indeed, the major part of optimizations only focus on climate change and thereby decrease the interest of LCA.

Limits linked to process simulation

Modeling complexities

An important barrier to the development of LCA coupled to process simulation software method is certainly complexity to represent: to modelize the biorefinery processes. Indeed, these models are still complicated to find in literature, but are more and more developed,[29,105,153–157] and it is not always possible to create each model before an assessment. Nevertheless, some wood biorefineries were originally pulp and paper industries, and changed to increase revenue by producing bioenergy and biomaterials in addition to wood, pulp, and paper products.[158,159] In these cases, the original processes – a Kraft process, for example – are often enhanced in order to change the activities. So, it can be useful to use Kraft process models from the literature.[160] Moreover, another fundamental issue is the difficulty to establish models which take into account the heterogeneity of biomass raw materials. Indeed, feedstocks are generally a mix of different species of biomass. Moreover, the major part of process simulation software was originally destined for the petrochemical industry. Consequently, they only consider liquid or gaseous flows. A major difficulty is then to model complex solid biomass feedstocks. To face this problem, Cohce *et al.*[161] worked on the gasification of palm oil shell. They worked with Aspen Plus®, which divides mass streams into three categories: mixed, solid, and non-conventional. Biomass is part of the third category. Non-conventional components are defined by supplying standard enthalpy of formation and the elementary composition (ultimate and proximate analyses) of the components may also be defined. This conversion of biomass into a mixture of carbon, hydrogen, oxygen, sulfur, nitrogen, and ash is used by Nikoo and Mahinpey[162] and Ramzan *et al.*[163] A similar approach is used by Miltner *et al.*[164] who consider biomass as a mixture of fixed carbon, water, and volatile compounds. To describe a solid, three properties are required: heat of formation, heat capacity, and density.[165] Another approach is to consider solid biomass as a high molecular weight hydrocarbon that is present in the Aspen library. This approximation permits to obtain the essential macroscale thermal, flow, composition, and pressure dynamics.[166]

Influence of operating conditions

As mentioned before, LCA coupled to process simulation tools is a powerful option to select, design, and optimize a process route with the most sustainable options. This method is useful as a decision-making tool for the choice of unit operations between several alternatives. For instance, this method could help to choose a lipid extraction method from biomass between different technologies, such as solvent extraction, supercritical carbon dioxide extraction, and others. Moreover, this optimization could also allow to study the influence of operating conditions on the environmental impact scores (and on social and economic aspects). Indeed, a change of operating conditions during the process simulation will lead to a change in the obtained mass and energy balances. Consequently, a change of the environmental LCA results will occur, too. So, it is possible to directly understand and study the sensitivity of the environmental impacts to the changes of operating conditions, such as pressure, temperature, and so on. Indeed, Azapagic[93] highlighted this influence with the assessment of volatile organic compounds abatement technologies at the end-of-pipe. In this study, different LCA were compared, with xylene flow rates changes (from 1000 to 20 000 m^3/h) and concentration changes (from 200 to 1200 mg/m^3 for xylene). Mery *et al.*[82] assessed the environmental impacts linked to operation conditions. Indeed, these functioning conditions make a significant contribution to the impacts of processes, and especially for ozonation processes. Moreover, Eliceche *et al.*[167] solved a multi-objective optimization with GAMS to determine the optimum operating conditions to apply to minimize the environmental impacts of an ethylene plant. They found that pressure and temperature could have a strong influence on several impacts, such as global warming. Another example of the influence of operating conditions is the case of microfiltration processes assessed by Tangsubkul *et al.*[168] Nevertheless, this practice is still not performed for biorefineries. For instance, Mesa *et al.*[169] worked on the restructuring of a biorefinery based on the use of sugarcane bagasse. The study intends to optimize furfural and xylose production. In this case, operating conditions are taken into account for the optimization. Indeed, models representing furfural variations induced by temperature, acid concentration, or reaction time were used. However, this optimization was focused on technical constraints, and therefore no LCA was achieved.

Limits linked to LCC and social LCA

One of the main problems to realize the LCC of a biorefinery is the fact that is an emerging sector. Consequently, costs undergo important fluctuations. Indeed, biomass feedstocks prices strongly vary.[103,134] Moreover, it is difficult to estimate with precision the infrastructure costs of a biorefinery installation, due to the lack of background on these new processes. Another crucial point concerns the selling prices of products and co-products, which will undeniably fluctuate during the following years, due to the increase of biorefining activities. Consequently, it is complicated to obtain reliable data to realize an LCC since the first design phases. In the same way, the realization of a social LCA will encounter the same difficulties concerning data collection. Finally, the absence of a common and harmonized framework for these two methodologies is a paramount obstacle to the development of these assessments.

Links with green chemistry

Previous section highlighted the fact that biorefineries seem to be the most appropriate and the most environmentally-friendly alternative to petroleum based refineries, on environmental and economic criteria (170). Moreover, Life Cycle Assessment, coupled to process system engineering tools such as process simulation software, or integrated into a global methodological framework with social and economic assessments, is a powerful tool to assess the sustainability of biorefineries.

To go further, it could be really interesting to use this methodology in synergy with other techniques used for sustainable development. Thereby, producing more sustainable products should be possible by applying green chemistry principles to biorefining processes, as announced by Clark *et al.* [23] In fact, some principles have already been put into practice such as the raw materials savings. Indeed, wastes from the food industry can be used as feedstocks for biorefineries. The possibility to create links with other fields and industries is particularly interesting and promising. Furthermore, some green chemical technologies could be employed in biorefining process routes, such as supercritical fluid extraction, microwave processing, or catalysis. The use of these technologies could lead to a more efficient use of renewable resources. Indeed, wood contains a large variety of interesting substances: terpenes, sterols, and others which are still not valorized in biorefineries. In the same idea, lignin is often underrated, due to its complex structure, [125] but microwave activation can be used to produce vanillin from lignin. [23] Other promising ways deserve to be more developed, such as process intensification, already used in the chemical industry. [52] Moreover, some green metrics are already used to assess processing routes based on biomass, and could be associated with LCA. [171] Indeed, Juodeikiene *et al.* [172] worked on the production of polylactic acid with biomass, and applied four paramount metrics: material efficiency, total energy efficiency, economic added value, and land use. The application of green chemistry to biorefineries could induce a substantial reduction of the environmental impacts and a maximization of potential profits. [173]

Conclusion

During the last few decades, LCA has been increasingly applied to industrial products. Nevertheless, these evaluations did not highlight the exact contribution of manufacturing activities to global environmental impacts. Consequently, LCA applied to industrial processes have been tested in many sectors, mainly to chemical activities. These new considerations permitted a complete and detailed comprehension of all the UOs included in a production process, i.e., the understanding of the influence of operating conditions and of the synergistic effects between the different unit operations. Nevertheless, this approach was only achievable on already designed processes, to obtain a sufficient amount of data essential to realizing the LCA. Therefore, process simulation software has been used to predict data and obtain mass and energy balances of the processes. The constant development of new biomass-based plants and the generalization of the application of LCA to processes presage significant changes in the industrial sector. Indeed, worldwide societies realize the necessity of a transition toward more respectful production practices.

The first part of the article is a literature review which underlined the different works and studies related to LCA of biorefineries. 39 publications have been identified and detailed. The review can be separated into three parts: LCA of biorefineries for feedstocks comparison, LCA of biorefinery process alternatives and LCA coupled to process simulation for process assessments.

In the second part of the paper, a new methodology for a sustainable eco-design of biorefining processing routes has been proposed. This promising way for improving consists in an integrated assessment of economic, environmental, and social considerations of biorefinery processes, on a life cycle perspective. Upstream of these analyses, a process simulator is used to facilitate data collection, for environmental LCA achievement. Finally, a multi-objective optimization of the process is performed, supported by a decision-making tool to identify the most sustainable designing way of a biorefinery process. Some of the main limits and ways for improving of this methodology have been identified and discussed. These locks can relate to the application of LCA to bio-based products, to the process simulation, or to the assessments of economic and social dimensions.

This new framework could facilitate and develop sustainable design of biorefinery processes and help to the construction of a more sustainable industry in the future.

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