



Levulinic acid biorefinery in a life cycle perspective

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Nowadays there is a strong urge to replace the fossil-based chemicals and fuels with biobased ones. In this context, the 7th principle of the green chemistry, the Sustainable Development Goals (SDGs) and the recent Safe and Sustainable by Design (SSbD) approach are the main references. Among the various biorefineries, lignocellulosic biomasses represent the most abundant resource to explore. Considering the vast plethora of useful molecules produced from lignocellulosic biomasses, levulinic acid embodies a potential starting material for the preparation of high value-added chemicals. This review explores the preparation of levulinic acid from lignocellulosic biomasses and its further valorization to high-value added compounds (γ -valerolactone, ketals and methyl/ethyl levulinate), considering the current state of the art of the available synthetic strategies, in a life cycle perspective considering the adoption of the life cycle assessment (LCA) methodology.

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Current Opinion in Green and Sustainable Chemistry 2024,
50:100963

This review comes from a themed issue on **Bioactive compounds (2024)**

Edited by **Khaoula (K) Khwaldia** and **Abennacer Boullilia**

Available online 22 August 2024

For complete overview of the section, please refer the article collection - **Bioactive compounds (2024)**

<https://doi.org/10.1016/j.cogsc.2024.100963>

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Keywords

Levulinic acid, Lignocellulosic biomass, Life cycle assessment, γ -valerolactone, Levulinate esters, Levulinate ketals.

Introduction

Currently, the transformation of biomasses and waste biomasses represent the most attractive alternatives to substitute the traditional chemical processes, mainly based on oil refining, for the preparation of chemicals, products, materials, and energy [1–3] particularly if waste biomasses are exploited. As a matter of fact, non-renewable fossil sources are still the main contributor to the worldwide energy and material demand and their over-consumption is still increasing with severe repercussions on environmental pollution and global warming [4]. The emerging biobased chemical industry branch is currently small compared to the entire manufactory [5], but its coverage is going to grow in the next years, as long as market can rely on new feasible green economy strategies [1]. Therefore, the scientific community is focused on two main objectives: discovering novel methods for processing biomasses to generate energy and chemicals and maximizing the value of the resulting molecules. Biomasses include a wide range of starting materials, such as crops and residues, agricultural, aquatic plants, wood, wood residues, vegetable oils and animal wastes [6]. Among these particular interest is devoted to residual and non-edible lignocellulosic biomasses (LCB) [7]. Indeed, LCB seems to become as a functional feedstock since they are abundant and well distributed worldwide resource, limiting inequalities and social conflicts [8]. Moreover, LCB are low-cost, easily available and non-competitive feedstock with the food industry [9]. LCB are generally composed of cellulose (35–50 wt%), hemicellulose (25–30 wt%), and lignin (15–30 wt%) and they can be exploited for the biofuel and chemicals production through physic-chemical transformation into platform molecules [10].

Among the wide plethora of chemicals obtained from LCB, levulinic acid (LA) has attracted high interest. According to U.S. Department of Energy (DOE) and National Renewable Energy Laboratory (NREL) LA appears as one of the 12 most promising platform molecules [11,12]. In 2019 the global LA market achieved \$27.2 million, and it is expected to reach \$60.2 million by 2030 [13].

In the last decades, manuscripts and papers about LA and its derivatives have been steadily increasing because of their potential industrial applications in several

sectors, including pharmaceutical and cosmetic manufacturing, agriculture and food industries, and chemical, polymer and fuel industries [9,14].

The presence of two versatile functional groups (i.e. carbonylic and carboxylic) on LA and levulinic esters (LEs), makes them very attractive and versatile molecules due to the variety of possible conversions and functionalization [6–15]. To date, several strategies to convert LA to green solvents, biofuels and platform chemicals have been reported [16]. Among these, in this review we want to focus our attention on LEs (in particular methyl and ethyl levulinate [15,17], diphenolic acid (DPA) [18], ketals [19–21] and γ -valerolactone (GVL) [22,23]. All the mentioned products can be considered attractive as they could replace (in part or in toto) products nowadays produced using fossil sources. In particular, LEs potentially have the largest markets: for example, ethyl levulinate provides a good blending option with fuels [24], ketals can be used as additives in ink and paint formulations, GVL [25] as additive for diesel blends, DPA as a replacement of Bisphenol A for the production of polyurethane foams [26].

Indeed, despite significant efforts have been spent into the synthesis of LA derivatives (the adoption of heterogeneous catalysts, the valorization of each component of biomass, the use of biomass-derived reagents, the adoption of co-catalysts in order to improve the selectivity toward the target product, the optimization of the main reaction parameters, the kinetic studies, the use of continuous flow reactor, the adoption of the catalytic transfer hydrogenation approach), a lack of knowledge about the environmental sustainability of these processes still needs to be overcome. For this purpose, life cycle analysis stands as a powerful tool to guide future developments in this context in view of large-scale development and in Table 1 are reported the main contributions. Life cycle assessment (LCA) is a standardized methodology (ISO 14040; ISO 14044) [27] able to contextualize punctual chemical and technological data within the wider view of the entire life cycle of a product or a process, from the extraction of raw materials to the end of life and consequent disposal of it (and its components) as a waste [28]. To ensure consistency, the LCA methodology is divided into four conceptual phases:

1. **Goal and scope definition:** The field of application is specified by identifying the system boundaries and the functional unit (FU). The system boundaries clarify what should be included in the study and what can be optional. The functional unit relates all input and output streams within the boundaries to a common reference unit, enabling model creation and comparison.
2. **Inventory analysis (or LCI: life cycle inventory):** This phase involves data collection. Using primary data is

highly recommended to construct an LCI that accurately reflects reality.

3. **Impact assessment (or LCIA: life cycle impact assessment):** Researchers choose standardized methods to evaluate the environmental performance of the created model. The quality of the data directly influences the reliability of the LCIA results.
4. **Interpretation:** This phase is crucial for assessing the LCIA results to identify critical issues and develop effective solutions to reduce the environmental impact.

Levulinic acid preparation from biomass in a life cycle perspective

As matter of fact, only few papers have been reported in literature so far concerning the adoption of the LCA within the LA biorefinery, and most of them deal with the preparation of LA from biomasses. LA can be industrially produced from both hemicellulose and cellulose; in details, the hydrolysis of hemicellulose yields a mixture of C5 and C6 sugars, while C6 sugars are majorly obtained through the hydrolysis of cellulose (Figure 1) [4]. Acid-catalyzed degradation of cellulose gives C6 sugars which are the main components of LCB. The C6 (mainly glucose) pathway involves the dehydration giving 5-hydroxymethylfurfural (HMF), going through the isomerization of glucose to fructose. As a result, the as-obtained HMF is subsequently hydrolyzed to LA [11]. The C5 pathway includes furfural as the first hydrolysis intermediate, which is consequently hydrogenated to furfuryl alcohol and hydrolyzed to LA [9] (Figure 1) [38]. Recent market data show that HMF has a market value of 1105\$/ton, with an overall production capacity of 54,000 ton/year [39], vs 1700\$/ton and 360,000 ton/year for furfural [40]. These data must be compared with the ones reported for levulinic acid, being 1349\$/ton and 20,000 ton/year [41]. By comparing the numbers, it is evident that the C6 platform can be considered more economically attractive being the price of the intermediate lower than the final product.

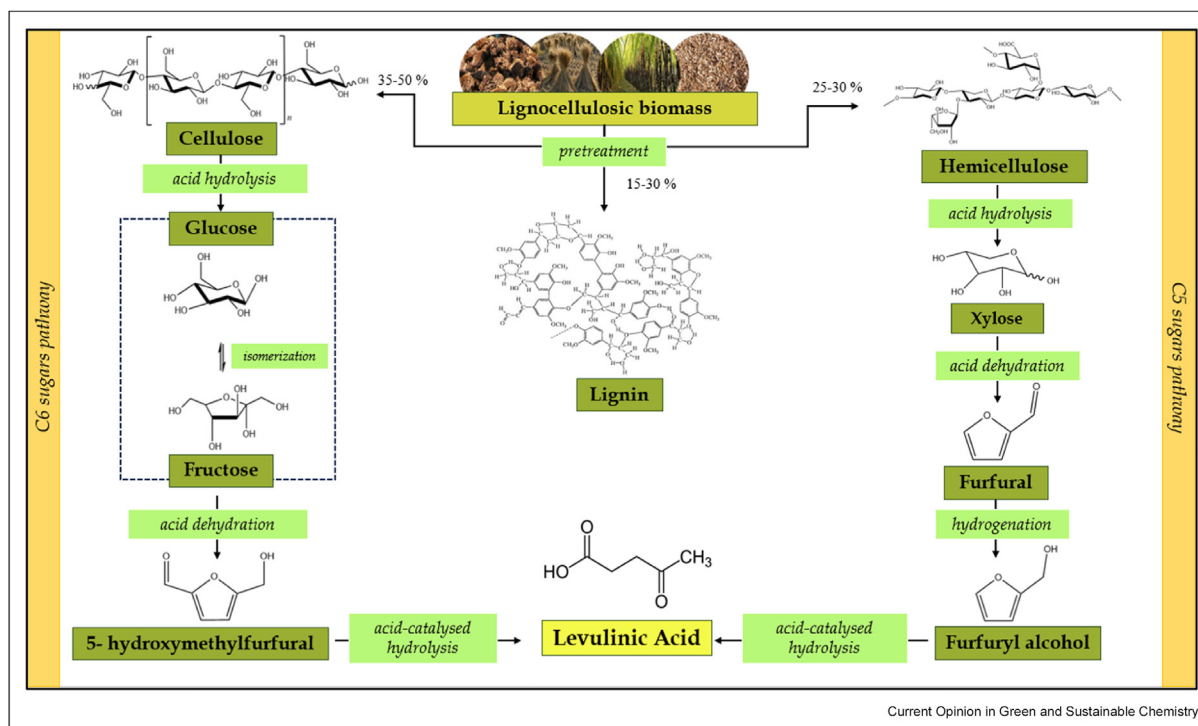
Isoni and coworkers [29] explored the levulinic acid preparation from agriculture residues (i.e., empty fruit bunches (EFB) and rice straw) as lignocellulosic feedstock. In that work both C5 and C6 sugars are converted into LA, formic acid, and acetic acid. The proposed cradle-to-gate LCA was carried out considering some relevant aspects and data for the life cycle inventory (LCI): different feedstock choices including cultivation and land use, logistics and storage, energy demands, CO₂-eq emissions, plant capacity (20 kton/year) and costs [29]. First, it was estimated that approximately 7 kg of biomass (glucan content 30–34 wt%) are needed for 1 kg of levulinic acid (*functional unit*) production. Also, three different LA isolation methods have been analyzed: direct distillation of the aqueous stream, and liquid–liquid extraction testing 2-methyl tetrahydrofuran (2-MeTHF) or methyl isobutyl ketone (MIBK). The

Table 1

Main LCA studies on LA and its derivatives proposed in the current study.

Raw material	Product	Functional Unit	Data source	Background database	Area of interest	System boundaries	Software	LCIA method	Reference
Empty fruit bunches and rice straw	Levulinic Acid	1 kg of levulinic acid	Literature	Unknown	Southeast of Asia	Cradle to gate	Unknown	/	[29]
Corn stover and rice straw	Levulinic Acid	100 ktons of levulinic acid	Literature	NREL, Ecoinvent	China, Us, Japan, Germany, Singapore	From farming activities up to the final product distribution	GaBi	/	[30]
Dried chips (residual wood)	Levulinic Acid	100 kg of <i>Pinus pinaster</i> (dried chips)	Experimental data	Ecoinvent	Europe	Cradle to gate	SimaPro	ReCiPe MidPoint	[31]
Almond shells	Levulinic Acid	0.066 g of Levulinic acid	Experimental data	Ecoinvent	Spain	Cradle to gate	/	PEF Guidelines	[32]
/	γ -valerolactone	10 g of γ -valerolactone	Experimental data	Ecoinvent	/	Gate to gate	SimaPro	IMPACT 2002+ V2.14/IPCC GWP	[33]
Residual <i>C. cardunculus</i>	Ketal-diester bioplasticizers	1 g of bioplasticizer	Experimental data	Ecoinvent	/	Cradle to gate	SimaPro	ReCiPe 2016	[34]
Rice straw	Methyl Levulinate (ML)	1 kg of ML	Pilot plant	Chinese Life Cycle Database (CLCD)	China	Cradle to gate	eFootprint	ReCiPe MidPoint, IMPACT 2002+, CML 2002	[17]
Corn stover	Ethyl Levulinate (EL)	1 t of EL	Pilot Plant	Ecoinvent	China	Cradle to grave	SimaPro	ReCiPe method	[35]
<i>Brassica carinata</i>	Ethyl Levulinate (EL)	1 ha of marginal land cropped with <i>B. carinata</i> for one year	Hypothetic case	Ecoinvent	South Italy	Cradle to gate	SimaPro	CLM 2001 and CED	[36]
Rice straw	Ethyl Levulinate (EL)	1 kg of EL	Simulation	Ecoinvent	Colombia	Cradle to gate	Open LCA v 1.10	ILCD 2011 midpoint + baseline method	[37].

Figure 1



Levulinic acid obtained through C6 and C5 sugars.

study has revealed that the use of 2-MeTHF required less energy demand than the other two methods. Lower energy requirements are closely linked to both reduced annual energy costs and decreased indirect greenhouse gas emissions. Moreover, a clear correlation between deforestation and the increase in CO₂ emissions has been demonstrated. In this context, rice straw could be considered an innovative lignocellulosic feedstock for a biorefinery process, as it has a lower impact on deforestation. However, looking ahead, the increasing global population could lead to a significant rise in rice demand and, consequently, a greater need for land available for agriculture. Therefore, attention should be paid to the potential deforestation associated with this phenomenon. Furthermore, LCA demonstrated that both rice straw and EFB are remarkably rich in silicon and potassium, thus biomass continue removing could cause on the long run mineral depletion and consequently infertility land issues. This problem could be got around using the aqueous stream deriving from the pretreatment of lignin favoring their reuse as potential fertilizer. Additionally, it has been shown that when the reference biomass (empty fruit bunches and rice straw) involves deforestation, the impact of the entire process in terms of GHG emissions can be up to 1600 times higher than in the most optimistic scenario (without deforestation practices). Further evaluations and a

redefinition of life-cycle boundaries are suggested to achieve a bio-designed and more sustainable process.

In a recent study of Khoo et al. [30], supply and distribution of 100 ktons of LA (functional unit) to China, United States (US), Germany, Japan, and Singapore are discussed. Considering the LA demand from chemical industries, corn stover and rice straw have been chosen as starting biomasses, as they are the main feedstocks in the U.S. and Asia, respectively. The study boundary encompasses all steps from farming activities to the final product distribution. All data were modeled using the software *GaBi* [42], and the following impact categories were identified as the most relevant: (a) Global Warming Potential (GWP) due to greenhouse gas emissions (GHGs) produced at farms, CO₂ uptake during crop cultivation, and GHG emissions during transportation; (b) acidification and eutrophication potential resulting from the use of fertilizers and emissions related to farming activities. It derives that paddy fields are the main contributors of greenhouse gases (GHGs), such as nitrous oxide (N₂O) and methane (CH₄). Additionally, the transportation of biomass by sea significantly contributes to the global warming potential (GWP). Consequently, farming activities are responsible for emissions of NO_x and NH₃ due to the use of N-fertilizer applications that could affect both eutrophication and

acidification. Additionally, land footprint highest values, related to the use of agricultural areas dedicated to grow crops, are recorded especially for India and Thailand. A qualitative evaluation of the study shows that scenarios involving the use of corn stover from the U.S. as feedstock are identified as having the lowest environmental impacts [30].

González-García and coworkers discussed the high environmental impacts associated with the pretreatment of LCB, in terms of energy requirements for the purification/conversion processes in the valorization of LCB to LA [31]. In this study, a cradle-to-gate LCA has been built setting 100 kg of dried chips (residual wood) as functional unit, using *ecoinvent* [43] as database and the software *SimaPro* to carry out the analysis [44]. The current LCA report covers all activities, from the production of raw materials to the final refining into high-value-added chemicals. The impact assessment step carried out through the Recipe Midpoint methodology displays that the amount of energy required for LCB acidic treatment represents the environmental hotspot of the process. In particular, the post-autohydrolysis phase for both the liquid and solid fractions necessitates a substantial amount of energy. This is primarily due to the operation of the reactor at 170 °C for 5 h and to the process of Acetosolv pulping (an organosolvent treatment that has been used to separate cellulose, hemicellulose, and lignin from lignocellulosic material by taking advantage of the higher affinity for the lignin oligomers to dissolve in organic solvents). Especially for post-autohydrolysis-solid subsystem the large amount of acetic acid consumed is accountable for around 99.8% of the whole process impacts. The current work paves the way for future research in which to focus on optimizing extraction techniques to reduce the impacts ascribed to large energy contribution.

In another work, it has also been reported LA preparation through H₃PO₄-assisted hydrothermal carbonization (HTC) together with the co-production of activated carbon (obtained through pyridine functionalization), at a laboratory-scale [32]. A life cycle approach in an attributional perspective [45] has been also applied to this innovative process. Herein, the functional unit is represented by the quantity of LA obtained at laboratory scale (0.066 g of LA per gram of almond shell) and the system boundaries cover the *cradle-to-gate* area. Three scenarios have been compared: reference scenario (A), which stands for the baseline process, the “*Max lab*” scenario (B), which contemplates the maximization of both the laboratory equipment capacity and the product yield, and the “*Improved scenario*” (C), which proposes all the technological improvements to overcome the critical issues derived from the LCA. In detail, the Max Lab scenario consists of the following operational adjustments aimed at reducing electricity consumption (spread over

multiple steps): 40 g of biomass, instead of 1 g, is washed using the same stirring plate; stove utilization is maximized; a 50 mL autoclave is replaced with a 1 L autoclave; the rotary evaporator used for liquid phase purification is utilized at its maximum capacity (2000 mL), whereas only 0.75% of its capacity is used in the reference scenario; and the washing and oven capacities have been increased. The Improved scenario has been upgraded by validating each modification at the laboratory scale. The changes considered in this scenario mainly involve reducing the duration of the liquid phase purification, washing cycles, and functionalization stages.

In the first scenario (Reference), electricity consumption is the main contributor to many impact categories, accounting for more than 45–80% (climate change, photochemical ozone formation, acidification, freshwater eutrophication, freshwater ecotoxicity, fossil resource use), followed by the use of pyridine, which significantly impacts both human carcinogenic toxicity and marine eutrophication (20.2% and 42.8%, respectively). The second scenario (Max Lab) is characterized by a reduction in energy use, as well as reductions in human toxicity and marine eutrophication by 20% and 40%, respectively. Nevertheless, the reduction in energy consumption does not significantly impact the overall environmental impacts, and the use of pyridine still significantly affects human toxicity and marine eutrophication.

The Improved scenario results in a 30% reduction in environmental impacts compared to the Max Lab scenario, except for those related to the use of pyridine, which remains the main contributor to environmental impacts. Furthermore, it was found that potential optimization during process upscaling could lead to a more significant reduction (30–60%) in environmental impacts while maintaining the same quality of the final product. In conclusion, although these results seem encouraging, they refer to an emerging laboratory-scale technology and are significantly affected by a high variability factor. In this regard, further investigation through a techno-economic analysis is suggested to provide an effective evaluation of the feasibility of the proposed process [32].

High value-added compounds derived from levulinic acid: a focus using LCA methodology

The efforts of the scientific community are addressed to develop an effective LA-based biorefinery, by making its derivatives of good economic value, sustainable and able to reduce the chemical industry’s reliance on petroleum [29]. Herein, we focused our attention on some of the most relevant LA-derived products, such as GVL, LA/LEs ketals, methyl levulinate (ML) and ethyl levulinate (EL).

GVL

GVL is among the most investigated green solvents due to its excellent chemical–physics properties and its preparation which involves the use of renewables. It has a low melting point ($-31\text{ }^{\circ}\text{C}$), a high boiling point ($207\text{ }^{\circ}\text{C}$), and a high flash point ($96\text{ }^{\circ}\text{C}$), thus resulting to be stored and transported and at the same time, it does not generate peroxide in the air and does not react with water at a temperature above $60\text{ }^{\circ}\text{C}$ for four weeks [46]. GVL serves as a solvent with extraction efficiency comparable to widely used polar organic solvents. It also boasts low toxicity ($\text{LD}_{50} = 8800\text{ mg/kg}$) and ecotoxicity and excellent biodegradability [47]. Specifically, it's defined as readily biodegradable, as it degrades $>60\%$ within 28 days [48]. GVL is a dipolar, aprotic solvent, with a relatively high dielectric constant ($\epsilon = 36.5$) and a high dipole moment of ($\mu = 4.30\text{ D}$). It is similar to solvents like N-methyl-2-pyrrolidone, dimethylacetamide, dimethylformamide, N,N'-dimethylpropyleneurea, acetone, and dimethyl sulfoxide. Consequently, it can find application in organic synthesis, industrial processes, and consumer products where these highly polar aprotic solvents are frequently employed. Thus, GVL is a suitable candidate for Heck or Negishi cross-coupling reactions, polymers synthesis (e.g. polyimides, polyethersulfones, polyacrylates, polyvinylchloride), metal-catalyzed arylations and alkenylations, halogenations, esterification, and pharmaceutical and cosmetic formulations [48]. In biomass transformation, GVL has been investigated as co-solvent for glucan saccharification, furfural production, and high-quality lignin recovery [34], cellulose and biomass hydrolysis and transformation [49–51].

The extraordinary versatility of GVL makes it one of the most important derivatives of LA [46]. The traditional hydrogenation of LA to GVL involves noble metal-based catalyst (Pt, Pd, Ru and Au) either homogeneous or heterogeneous and a hydrogen source [52].

Moreover, the LA hydrogenation by either external H_2 gas or by organic hydrogen donors (such as formic acid or alcohols) through a catalytic transfer hydrogenation (CTH) over non-noble metal catalysts has been explored on laboratory scale. Therefore, future research aims to the development of green catalysts (non-noble metals, mild conditions) on large-scale for this kind of process [46].

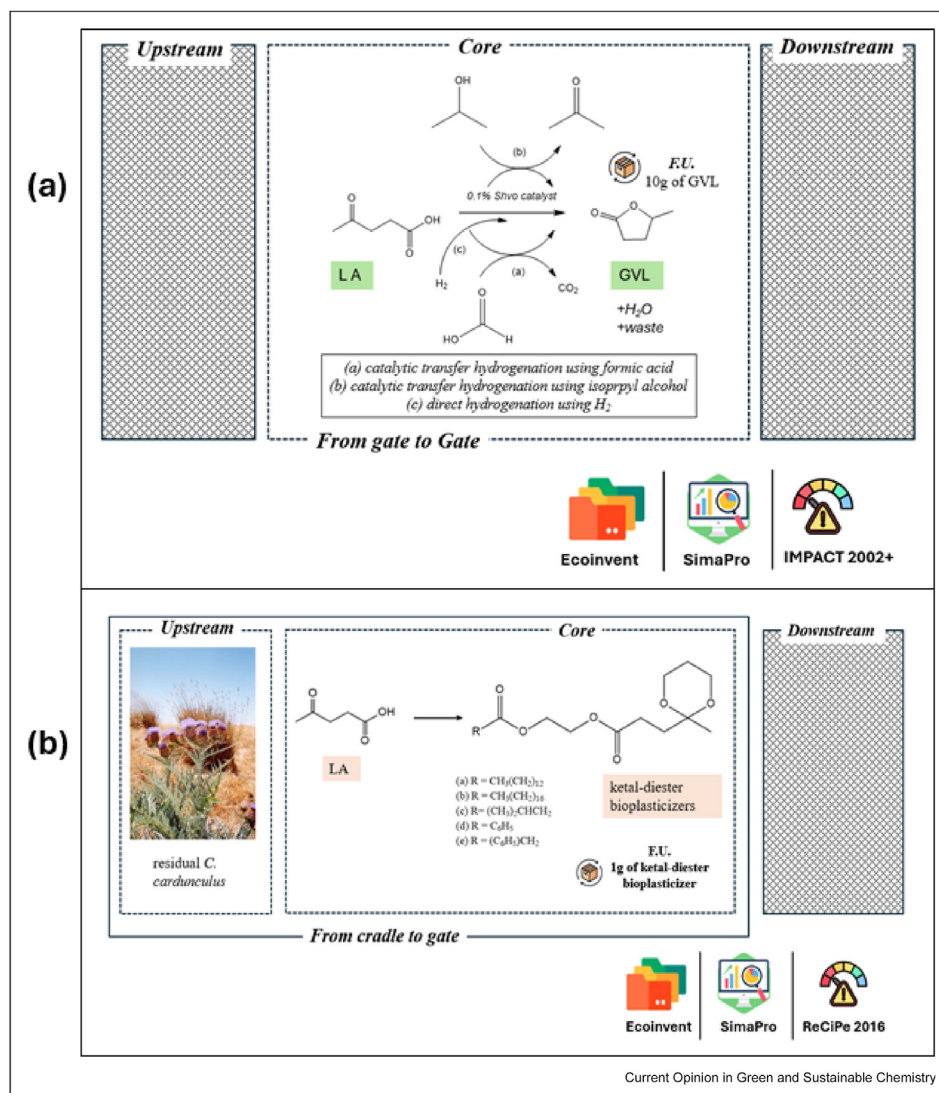
In a recent study, a LCA *gate-to-gate* has been carried out with the scope to evaluate the environmental impacts associated to different Shvo-catalysed hydrogenation pathways of levulinic acid to give γ -valerolactone. In detail, three different hydrogenation pathways - (a) transfer hydrogenation with formic acid or (b) with isopropyl alcohol, (c) direct hydrogenation with H_2 - have been modelled in *SimaPro V8* [44] and the impacts

have been calculated using the *IMPACT 2002+ V2.14* [53] method choosing 10 g of GVL product as functional unit. The environmental impacts related to the synthesis of LA (upstream) were excluded because they are too specific to the location or feedstock. Similarly, the 'end-of-life' scenario (downstream) is left undefined, as gamma-valerolactone (GVL) has applications in several fields. The analysis considers damage to human health (including human toxicity, respiratory effects, ionizing radiation, ozone layer depletion, and photochemical oxidation), ecosystem quality (both terrestrial and aquatic ecotoxicity), climate change related to greenhouse gas emissions, and resource depletion, which includes the sum of energy derived from non-renewable feedstocks. The results reveals that the total electricity consumption and the catalyst synthesis are the main contributors to the environmental impacts for all the investigated reactions. Moreover, assuming a quantitative conversion of LA, the most impactful process resulted to be the pathway b, employing isopropanol as reducing agent, followed by formic acid and H_2 (isopropanol \gg formic acid $>$ H_2). Several ways to reduce catalyst impacts are proposed. Firstly, the potential for catalyst recycling was assessed to minimize the impact of catalyst synthesis. Although recycling the Shvo catalyst has been shown to be incompatible with LA due to deactivation caused by co-produced water, it could be explored for other reactions. The benefit in terms of impacts was estimated by dividing the GWP value associated with catalyst synthesis by the number of catalytic cycles. This evaluation indicated that 147 cycles are needed to reduce the impacts to below 1%. Furthermore, another solution could involve catalyst immobilization to facilitate simple catalyst separation. This approach could reduce the environmental impact associated with the distillation purification step by 31%. However, immobilization presents several drawbacks, such as an additional synthesis step, catalyst decomposition due to water sensitivity, and potentially lower-purity GVL. Finally, reducing the reaction time could be another way to lower environmental impacts. LCA results showed that shortening the reaction time from 5 h to 3 h could result in a significant decrease of 0.5 kg CO_2 eq. per 10 g GVL, corresponding to a 7% reduction [33]. The process flowchart is shown in Figure 2a.

LA/LEs ketals

Levulinic ketals are promising chemicals with potential applications as additives for biofuels and as building blocks for producing plasticizers and surfactants [54]. The synthesis of levulinic ketals is generally carried out through a direct Fischer esterification (e.g. in presence of an alcohol under acidic conditions). Unfortunately, the esterification side-reaction becomes competitive under such conditions due to the bifunctional nature of LA, leading to the formation of both the desired ketal and ester byproduct [55].

Figure 2



Process flowcharts for the LCA of GVL obtained from LA through three different pathways (panel a) and for the LCA of ketal-diester bio-plasticizers production from LA (panel b).

The synthesis involves strong homogeneous mineral acids like sulfuric, hydrochloric, and phosphoric acid as catalysts even though their use is associated with some well-known negative issues such as the non-recyclability and unsafety [56].

A cradle -to- gate LCA of bio-plasticizers obtained from the reaction of LA with five different fatty acids (e.g. myristic, phenylacetic, benzoic, and isovaleric acids), has been recently reported [34]. In this work, 1 g of each bio-plasticizer was selected as the functional unit for their environmental impact comparison. The inventories have been modeled using *SimaPro* [44] while *ReCiPe 2016* [57] was used for the life cycle impact assessment (LCIA). The system boundaries include

crop production, biomass pretreatment, LA preparation through microwave-assisted acid-catalyzed hydrolysis, and the purification step. Additionally, the transformation of LA into the five ketal-diester derivatives is discussed. The reactions are schematized and illustrated in Figure 2b. The environmental impacts related to these processes are not competitive with those associated with commercially available phthalates and bio-plasticizers. This result is explained by the impacts evaluated at a laboratory-scale process. In fact, lower environmental impacts are generally associated with pilot or industrial-scale production. Single-score indicators obtained through endpoint analysis showed that, in all cases, the most significant categories are global warming and human health. In particular, human

health accounts for 45% of the impacts for all the products, with the primary contributor (approximately 91%) being fossil-derived carbon dioxide. The ketal diester deriving from a stearic acid precursor resulted in the one characterized by the lowest environmental impacts among those taken in account in the analysis. Furthermore, the research has delved into exploring the effects associated with the preparation of 1 g of the current ketal diester. It is evident that the primary factors contributing to its impacts are attributed to the diester derivative itself, the energy consumed during the heating process, and the management of waste generated from the workup.

Methyl levulinate

Methyl levulinate is the smallest LA derivative. It is largely used in a wide range of relevant fields, including pharmaceutical, fuel additive, solvents. Its singular molecular structure makes it very similar to the biodiesel. In this sense, adding ML to biodiesel can actually improve the cleanness of fuel combustion, and the resulting new type of mixed fuel shows excellent lubricating ability, flash point stability, and low temperature fluidity [7].

LEs can be directly obtained from LCB by one-pot acid alcoholysis, involving mineral or solid acids, where the latter are favored over the first concerning the well-known problems associated with their use as equipment corrosion and pollution issues. Moreover, mineral acids may affect the selectivity favoring the degradation of the intermediates (e.g. glucose) and the formation of humins [58]. It has also been reported that the formation of dialkyl ethers can be limited by using solid catalysts other than working at very low mineral acid concentrations [59]. Despite this, the performances of homogeneous systems are still generally superior to those of heterogeneous ones and more robust and highly active solid catalysts need to be developed [58]. The opportunity to tune acid-base composition and strength, hydrophobicity/hydrophilicity, and the surface area/porosity is fundamental to develop new and more efficient catalysts for the one-pot acid alcoholysis of LCB. As a result, most of the scientific community efforts have recently spent in the design of solid acid catalysts such as zeolites, metal oxides and acidic ion-exchange resins [60].

A LCA of ML production from rice straw in a *cradle to grave* boundary was reported in literature [17]. This study was developed considering an existing biorefinery settled in China. The scope of the study is to identify the bottleneck of the process, that is the step associated with most of the impacts. The analysis has been carried by using the software *eFootprint* and the database *Chinese Life Cycle Database (CLCD)* [61]. The functional unit for this life cycle model is set as 1 kg of ML (purity >98 wt %).

Energy conservation and emission reduction have been estimated by using *Aspen Plus®* [62], while an economic allocation is very difficult to apply considering the ML small market size. The process is summarized in Figure 3.

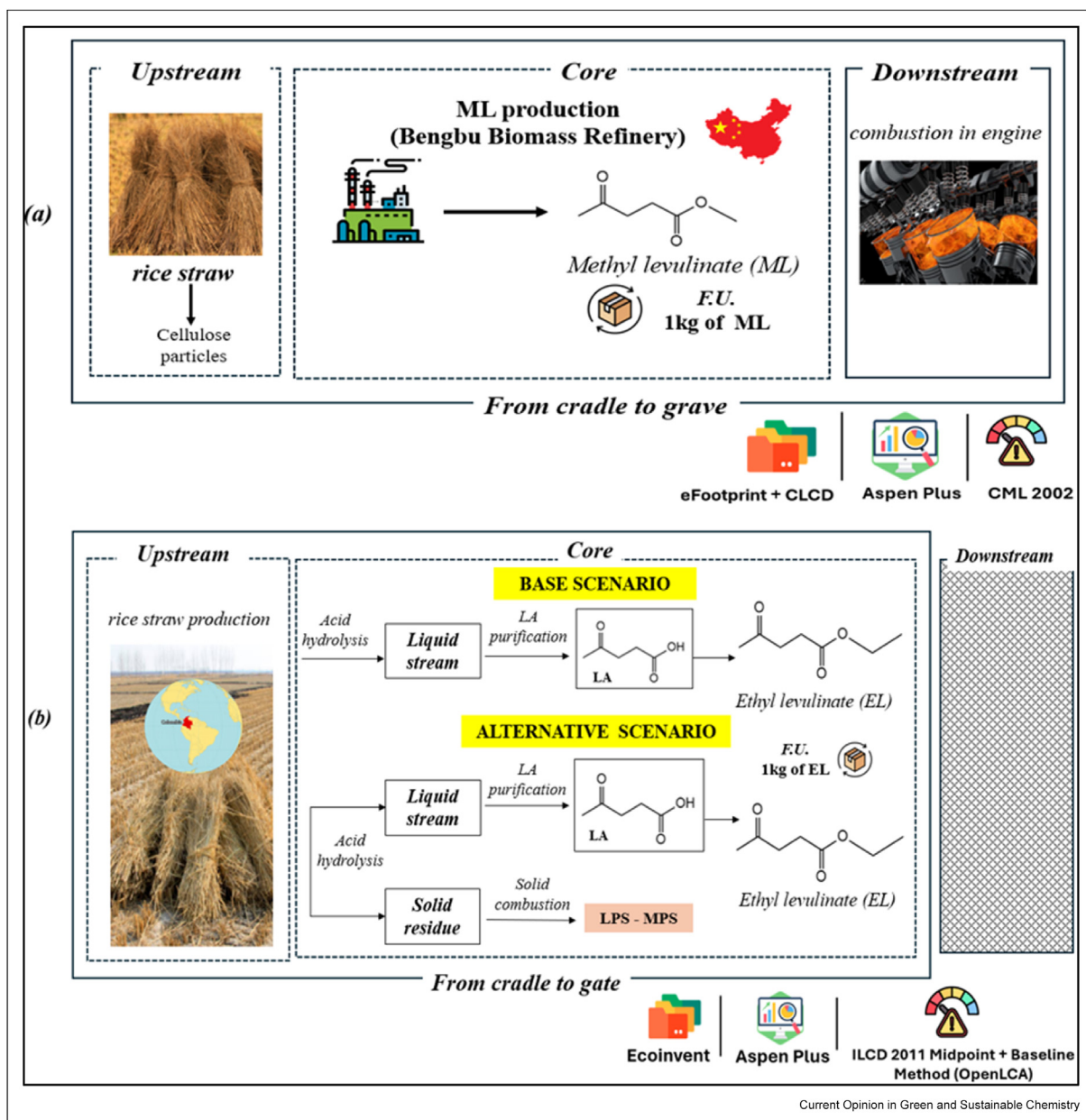
Results showed that impacts related to GWP, primary energy depletion (PED) and water usage (WU) are significantly high. In details, environmental impacts of the life cycle of ML mostly come from electricity, steam, methanol, and sodium hydroxide, and it is worth noting that the cellulose supply step alone contributes approximately half of the total GWP and PED. Considering the potential use of ML as fuel additive, a comparative life cycle study between ML and diesel has been also proposed to evaluate if ML has the potential to reduce emissions compared to diesel. Also in this case, the results are quite encouraging because it has been concluded that, when a local database is used, the biomass-based fuel (ML) has proven able to reduce the GWP by approximately 16%–29% compared to the fossil diesel. Nevertheless, this result shows the opposite trend when a non-local database is selected. Additionally, the study proposes several interventions aimed at reducing impacts, such as the potential energy conservation, thermal efficiency and the use of biomass electricity. Moreover, if hemicellulose is incorporated in the model for its application in future cycles, impacts are expected to decrease [17].

Ethyl levulinate

Ethyl levulinate is listed among the most interesting LA derivatives because of its several utilizations as in fragrances and in the flavorings, solvents and plasticizers, or as a blending component in biodiesel [63]. EL can be obtained through esterification of LA with ethanol or from the alcoholysis of LCB or cellulose. Alternatively, EL can be also produced from furfural, combining hydrogenation/transfer hydrogenation and alcoholysis reactions [64–67].

The EL application as a biobased diesel additive is also known. Only few works have reported a LCA study for producing EL from biomass. For instance, Wang [35] reported a cradle-to-grave LCA to produce 1 ton of ethyl levulinate (EL) (functional unit) from cornstarch, based on a representative EL plant located in Henan, the largest agricultural province in China. The Ecoinvent database and SimaPro software were used to assess both energy consumption (EC) and greenhouse gas (GHG) emissions. The entire process is organized into three subsystems: feedstock collection (upstream), EL production (core), and EL use (downstream). Energy consumption sources were not considered, as they were found to be negligible throughout the process, and cornstarch was assumed to be a waste product of corn production. It is worth noting that cornstarch has significant market value and can be used as a raw material for

Figure 3



Scheme of cradle to gate study of ML production in Bengu Biomass Refinery (China) (a) and LCA scheme of EL production from Columbian rice straw comparing "base" and "alternative" scenario (b).

other industries. Additionally, CO₂ absorption and emissions for each step were included in the study. The total EC was found to be 109.9 GJ per functional unit, with 104.1 GJ of that coming from biomass energy. The EL production stage accounted for the highest EC, representing 96.8% of the total, with 97.8% of this being biomass energy. In terms of GHG emissions, the overall global warming potential was 2.34 kg CO₂-eq/kg, mainly due to NO_x emissions during the EL production stage. Notably, a large amount of CO₂ is fixed during the

cornstalk growth, which offers a significant opportunity for GHG emission reduction. The EL production and utilization stages account for the highest GHG emissions in the LCA, representing 53.4% and 44.5% of the total positive GHG emissions, respectively.

Moreover, Fiorentino [36] discussed the production of EL from *Brassica carinata*, chosen as a suitable crop for a biorefinery located in Campania, Southern Italy. The study aimed to provide an environmental, energetic, and

economic assessment of the production of biodiesel and ethyl levulinate as the main products of the Biofine process, which involves converting the oilseed crop (*B. carinata*) into these value-added products. The functional unit was set as 1 ha of marginal land cultivated with *B. carinata* for one year. For the life cycle inventory (LCI) phase, the background dataset was assembled using data from Ecoinvent, especially for the upstream process, and materials and energy items were selected to match the Campania region as closely as possible. The life cycle impact assessment (LCIA) results, obtained using CML 2001 and Cumulative Energy Demand (CED), referred to the following macro-categories: Abiotic Depletion Potential (ADP, in kg Sb eq), Acidification Potential (AP, in kg SO₂ eq), Eutrophication Potential (EP, in kg PO₄³⁻ eq), Global Warming Potential (GWP, in kg CO₂ eq), Human Toxicity Potential (HTP, in kg 1,4-DB eq), and Photochemical Oxidation Potential (POP, in kg C₂H₄).

The normalization step showed that fertilizers, especially ammonium sulfate and nitrate, are the major contributors to each category, with abiotic depletion and global warming being the most impacted categories. Specifically, the entire agricultural step is responsible for 70% of the total global warming impact, with nitrogen fertilizers accounting for about 63% of the total emissions. CED analysis indicated that 60% of the cumulative energy demand is due to lignocellulosic residues used as a heat source. Thus, the agricultural phase is the hotspot of the entire supply chain and requires improvements to reduce fertilizer use. The Biofine process provides an energy saving of between 11 and 33 kton of oil equivalent per year compared to the conventional route, which involves obtaining EL from starch or sugar, a very energy-intensive process.

In conclusion, the study highlights the feasibility of a biorefinery-oriented system that utilizes raw materials and converts them into value-added products. It also identifies potential improvements needed to enhance profitability in terms of both environmental and economic benefits.

A cradle-to-gate life cycle assessment of 1 kg of EL obtained from Colombian rice straw has been also reported [37]. This study consists of a comparison of two scenarios, where the “base scenario” refers to the production of EL from rice straw via acid hydrolysis. The system boundaries include LA purification and EL preparation by esterification reaction, using fossil fuel to cover all the energy demand for the overall process. System boundaries also include the manufacturing of chemicals, catalysts, cultivation stage, use of energy, and transport of biomass. The “alternative scenario” includes the aforementioned conditions, but it considers (a) an increase of paddy rice yield (from 4.97 t/ha to 5.7 t/ha, considering the maximum for rice cultivation in Orinoquia region),

and (b) the use of the residual solid to produce low pressure steam (LPS) and medium pressure steam (MPS) as resources to supply the energy demand. *Aspen Plus*® [62] and ecoinvent [43] have been used (Figure 3). Mass allocation has been performed and solid residue was initially considered as “avoided product”.

The highest impact for the *base scenario* is the one related to the acid hydrolysis stage, requiring a huge energy demand, and in this context the fossil fuel-derived steam is the main contributor. Subsequently, the second highest impact is related to the requirements of paddy rice water and to the amount of water necessary for acid hydrolysis. On the other hand, the *alternative scenario* is associated with remarkable reduction for several impacts as climate change, photochemical ozone formation, acidification, ozone depletion, water resource depletion and freshwater eutrophication.

In fact, paddy rice fields are the main contributor of anthropogenic CH₄ emissions, while rice straw production brings the highest contribution to marine eutrophication, terrestrial eutrophication, and water resource depletions. In detail, emissions of NO_x associated with use of nitrogen fertilizers are the main responsible for environmental impact. Moreover, a considerable amount of water necessary for rice cultivation accounts for water resource depletions. An economic analysis displayed that EL from RS results to be competitive within the current EL market size, as the environmental impacts in terms of GWP (2.71 kg CO₂-eq/kg EL) are similar to that reported for current plants in China from corn (2.34 kg CO₂-eq/kg EL). Nevertheless, more studies are needed to assess the logistic and cost deriving from biomass (RS) transportation to plants and, in the second place, the availability of raw materials could represent a limiting point for the implement of this method on a large scale.

Conclusion and future perspectives

With this contribution an overview of the use of LCA tool to address the environmental impacts related to the LA production from biomasses and its further valorization to GVL, LA/LEs ketals, methyl and ethyl levulinate has been provided. However, there is an urgent need of LCA-based works comparing the traditional routes for LA preparation and valorization with the newly developed ones, often based on the use of heterogeneous catalysts instead of homogeneous ones. In summary, considering the existing publications and identified knowledge gaps, we propose several predominant needs for the scientific community:

- a comparative LCA study evaluating the preparation of LA from C5 and C6 sugars is essential
- a comparative LCA study to identify the environmental impacts related to the preparation of LEs from LA or directly from biomasses alcoholysis

- the adoption of LCA methodology also for the preparation of other LA derivatives as DPA, levulinates (in addition to ML and EL) and GVL-RP

Furthermore, the LCA approach is the key to develop hotspot-driven research of existing processes and to identify the bottleneck steps able to direct new research projects and directions [68].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors are grateful to Italian Ministero dell'Istruzione dell'Università e della Ricerca for the financial support provided through the LEVANTE project PRIN-Bando 2020, Prot. 2020CZCJN7. This work is part of the funded LEVANTE project, which involves five research units. All the authors have made substantial contributions to the preparation of this critical review, including conceptualization, writing, bibliography research, revision, and supervision.

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A clear focus on the need of LCA-base manuscripts.