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Chapter

Lactic Acid Production from Lignocellulosic Biomass

Asfaw Gezae Daful, Marie Loridon and Meegalla R. Chandraratne

Abstract

This chapter presents bio-based lactic acid production process from lignocellulosic biomass. Bio-based chemicals can replace the chemicals that we usually get from petroleum-based resources, and they are used to produce cleaners, solvents, adhesives, paints, plastics, textiles, and many other products. Lactic acid is one of such candidates of bio-based chemicals with important applications in various industrial sectors such as the chemical, pharmaceutical, food, and cosmetics industries, where its demand is steadily increasing. It is also an essential building block for numerous commodity and intermediate-biobased chemicals making it as a suitable alternative to their fossil-derived counterparts. The bioconversion process of transforming lignocellulosic biomass into lactic acid consists of four primary stages. Initially, pretreatment is performed to enable the utilization of all C₅ and C₆ sugars by the selected microorganism. These sugars are then hydrolyzed and fermented by a suitable microorganism to produce either L- or D-lactic acid, depending on the desired stereochemistry. Finally, the lactic acid is separated and purified from the fermentation broth to obtain a purified product. The promising method for the industrial production of bio-based lactic acid will be of continuous simultaneous saccharification and fermentation in a gypsum-free process using Mg(OH)₂ as neutralizer, followed by reactive distillation for purified lactic acid production. The *cradle-to-gate* life cycle assessment model for the biobased lactic acid production process indicated that the about 80–99% of the environmental burdens of most of the environmental impact categories can be reduced compared with its equivalent fossil-based lactic acid, making biobased lactic acid environmentally superior to the fossil-based lactic acid.

Keywords: lactic acid, biomass, bioconversion, life cycle assessment (LCA), environmental impacts

1. Introduction

Lactic acid (LA), the simplest hydroxy carboxylic acid with IUPAC name of 2-hydroxypropionic acid and a molecular formula CH₃CH(OH)COOH, is a bulk chemical with two optically active *enantiomers* (D(–) and L(+)), depicted in **Figure 1**, which has wide industrial applications in the food, chemical, pharmaceutical and health care industries [1–4]. The L(+) isomer is preferentially used for food and pharmaceutical

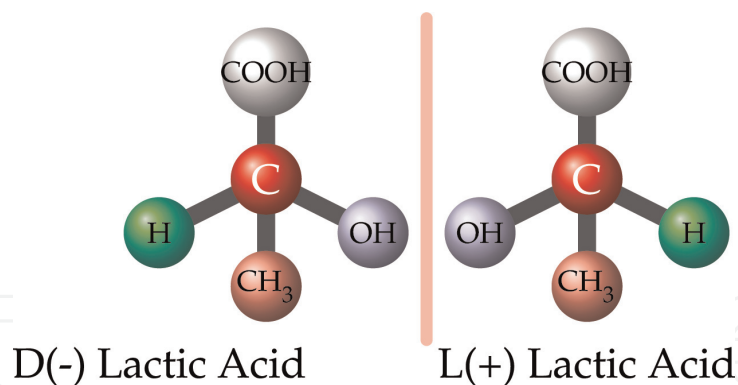


Figure 1.
Two stereoisomers (*D*(-) and *L*(+)) of lactic acid.

applications, being the only lactic acid isomer produced in the human body [5]. Lactic acid can be used as building block for a multiple of commodity and intermediate chemicals [3, 6, 7], such as acrylic acid, lactate esters, 1,2-propanediol, pyruvic acid, acetaldehyde, 2,3-pentanedione, ethanedioic acid, and polylactic acid (PLA), which is a biodegradable plastic suitable for packagings. Different applications of lactic acid can be either as final product or as feedstock for other processes like in food and cosmetics industries. PLA may be a suitable alternative to oil-derived plastics and has already a global market demand of approximately 10^5 metric tonnes per annum and is anticipated to grow by at least 28% per annum until 2025 [1, 8]. Low-molecular-weight PLA bioplastics can replace polymers such as polyethylene and polyethylene terephthalate, while high-molecular-weight PLA can replace polystyrene.

Lactic acid can be produced either by anaerobic fermentation [3, 9–11] from various sources, including whey, starch crops, sugar crops, and lignocellulosic materials, or by chemical synthesis [5, 10, 12–15] from fossil resources. The chemical synthesis pathway [5] produces an optically inactive *racemic* mixture of the L and D isomers, while the anaerobic fermentation pathway generally yields optically pure L or D isomer, depending on the microorganism used [1].

2. Production of lactic acid

Microbial fermentation and chemical synthesis are the two industrially important methods for lactic acid production as depicted in **Figure 2**. A *racemic* mixture of DL-lactic acid is produced by a chemical synthesis from fossil sources, while an optically pure D(-) or L(+) lactic acid is produced using microbial fermentation. Furthermore, microbial lactic acid fermentation offers several key advantages over chemical synthesis. First, the utilization of renewable feedstocks reduces dependence on non-renewable petrochemical resources and contributes to a more sustainable and environmentally friendly production process. Second, microbial fermentation enables the production of optically pure lactic acid, as either D(-) or L(+) enantiomers. Third, fermentation processes generally operate under milder conditions compared to chemical synthesis. They require lower energy input in terms of temperature and pressure, resulting in reduced energy consumption and associated costs. Finally, it can utilize a wide range of feedstocks, including sugars from various biomass sources, agricultural by-products, and even waste streams. This flexibility allows for the utilization of

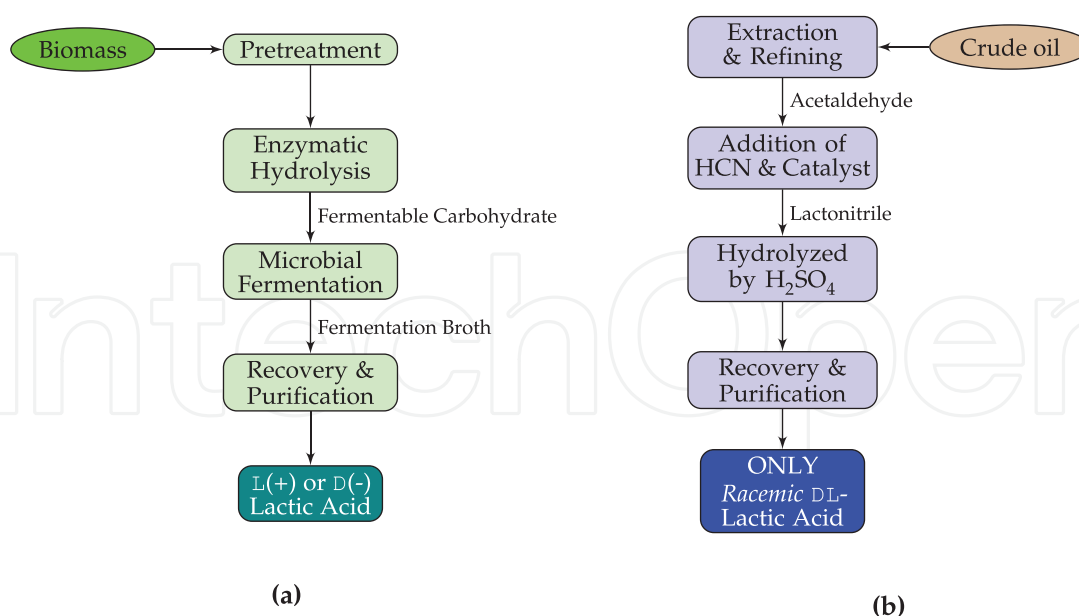


Figure 2. An overview of LA production processes: (a) microbial fermentation from renewable resources and (b) chemical synthesis from non-renewable resources.

diverse and readily available substrates, contributing to a more sustainable and cost-effective production process.

2.1 Renewable resources for lactic acid

Lactic acid's demand has been rising due to its increment in a wide range of applications, aiming on sustainability the utilization of low-cost non-food biomass materials for its production. Given its availability, and low cost compared to refined sugars, lignocellulosic biomass is a promising source for sustainable lactic acid production. Nevertheless, due to its complexity, it is still challenging to commercially use lignocellulose for lactic acid synthesis due to the recalcitrance of the major constituents of lignocellulose for bioconversions [10, 16, 17]. The bioconversion processes for producing lactic acid from lignocellulosic biomass, depicted in **Figure 2a**, includes four main steps [18]: (a) pretreatment [19]—breaking down the structure of the lignocellulosic matrix, (b) enzymatic hydrolysis—depolymerizing lignocellulose to fermentable sugars, such as glucose and xylose, by means of hydrolytic enzymes, (c) fermentation—metabolizing the sugars to lactic acid using homolactic acid strains [20–22] and (d) separation and purification of lactic acid—purification of lactic acid to meet the standards of commercial applications.

2.2 Pretreatment

Lignocellulosic biomass are composed of cellulose, $(C_6H_{10}O_5)_n$, (40–50%), hemicelluloses, $(C_5H_8O_4)_m$, (25–35%) and lignin $[C_9H_{10}O_3(OCH_3)_{0.9-1.7}]_x$, (15–20%) in an intricate structure where the components are rigidly associated through non-covalent bonds and covalent cross-linkages along with minor amounts of other compounds such as proteins, ash, and pectin. The highly polymerized phenolic lignin encrusted on the crystallized cellulose and hemicellulose polymer matrix causes challenges in the conversion processes as shown in **Figure 3**. The main bottleneck in utilizing such

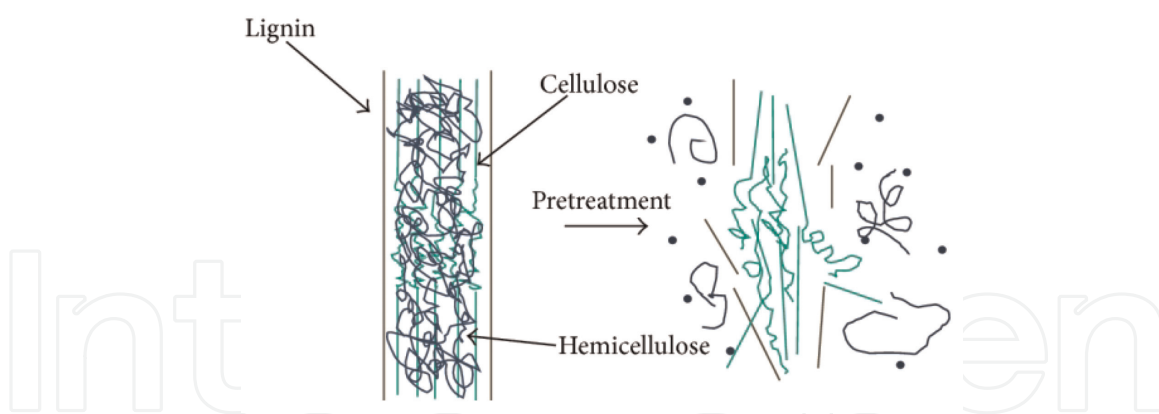


Figure 3. Schematic of the role of pretreatment in the conversion of biomass into its constituents, cellulose, hemicellulose, and lignin.

lignocellulosic biomass for bioproduct production is its complex, hierarchical, and recalcitrant nature. There are various pretreatment techniques that are classified as physical, chemical, physicochemical, and biological processes. The pretreatment step is required to increase the accessibility of the carbohydrate polymers by enzymes or bacteria/organism, where the enzymes depolymerize the polymer present in the lignocellulose, making them available for conversion of biomass to biofuels and value-added chemicals *via* fermentation. The size of the biomass feedstock is reduced first by milling to increase its surface area so as to increase hydrolysis efficiency. The main purposes of pretreatment are to condition the cellulose to increase its susceptibility to cellulase enzymatic digestion and hydrolyze the hemicellulose structural polysaccharides to oligomeric and monomeric sugars. Given the highly crystalline structure of cellulose that is embedded in a matrix of polymers-lignin and hemicellulose, pretreatment [18, 19, 23] is a very decisive step to overcome the recalcitrance of the lignocellulosic biomass to separate the cellulose from the matrix polymers and to make it more accessible for enzymatic hydrolysis. Various types of pretreatment have been developed, including physical (mechanical, milling, extrusion), physicochemical (steam explosion pretreatment, hydrothermolysis, wet oxidation, ammonia fiber expansion), chemical (dilute acid, alkaline, ionic liquids), and biological methods (microorganisms, enzymes). In this chapter, steam explosion [24–27] pretreatment will be discussed, which is one of the viable technologies and has been explored extensively in the recent years.

2.2.1 Steam explosion

Steam explosion is one of the most commonly employed and effective pretreatment methods, which is typically a combination of both mechanical forces and chemical effects applied to lignocellulosic biomass. Steam explosion is a process in which lignocellulosic biomass is treated with steam at a temperature of 160–250°C under high pressure (0.69–1.5 MPa), for a very short period of time, and the lignocellulosic biomass then undergoes an explosive decompression, which causes a estrangement in its rigid structure [25, 28]. Steam is driven out of the reactor through a nozzle by inductive force after condensing at high pressure and “wetting” the lignocellulosic material. At this point, various processes take place such as the condensed moisture evaporates as a result of pressure reduction, lignocellulosic matrix desegregation

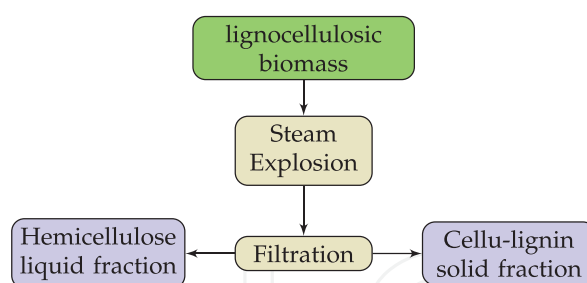


Figure 4. Schematics of steam explosion pretreatment of lignocellulose biomass and separation of the hemicellulose liquid and cellu-lignin solid fractions by filtration.

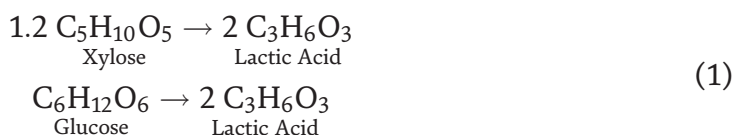
occurs, and breaking down *inter*- and *intra*-molecular linkages [25–27, 29]. The cellulose bundles are defibrillated by the sudden release of pressure, which makes it easier for enzyme hydrolysis and fermentation to access the cellulose. In addition, the high-temperature treatment causes the acetyl groups to hydrolyze, and the acetic acid that is then released catalyzes the hydrolysis of polysaccharides, primarily hemicelluloses, in a process known as *auto-hydrolysis* [25]. The solid cellulose and lignin network, cellu-lignin fraction, will be separated from the dissolved hemicellulose solution by filtration, as shown schematically in **Figure 4**.

2.3 Fermentation and purification processes

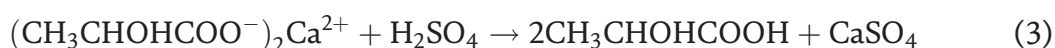
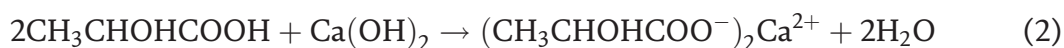
The hemicellulose liquid fraction and the cellu-lignin solid fraction are separated by filtration following the steam explosion treatments. For the purpose of removing sugars from the solid residues, the cellu-lignin solid fraction is washed. The hemicellulose liquid fraction (mainly xylose and other C₅ sugars) and the cellu-lignin solid fraction (mainly C₆ sugars) are used to produce lactic acid using various process methods. Lactic acid is produced from the liquid fraction of hemicellulose by simple fermentation, while cellulose and any remaining hemicellulose are hydrolyzed to produce fermentable monosaccharides from the cellu-lignin solid fraction to produce lactic acid using selected strains, which is known as a simultaneous saccharification and fermentation (SSF) [1, 9]. Acid-tolerant lactic acid bacteria were recently reported that can grow and ferment at pH 5.0 and at higher temperatures up to 60°C that are optimal conditions for cellulose hydrolysis by fungal enzymes. Such new isolates produce L(+)-lactic acid as the main fermentation product during the SSF processes with very low levels of cellulase [1, 30].

Lactic acid bacteria, particularly *Lactobacillus* spp., can ferment glucose (C₆ sugars) derived from the cellu-lignin solid fraction, which contains mainly C₆ sugars with some amounts of xylose (C₅ sugar) that is unfermentable by most lactic acid bacteria.

Lactococcus lactis IO-1 [31] and *Enterococcus mundtii* [32, 33] are the two common strains fermenting xylose to L(+) lactic acid, while *Lactobacillus pentosus* strains are for fermenting C₆ sugars [5, 10]. *Escherichia coli* is a candidate able to ferment all biomass-derived C₅ and C₆ sugars into L(+) lactic acid with high yields and optical purity, with minimal nutrient requirements, see Eq. (1) *Escherichia coli* B, WL204 [22], unlike the heterofermentative pathway which produces both acetic and lactic acids, is homofermentative genetically engineered strain to produce acetic acid free lactic acid with a yield of 90–97%, and an optical purity of 99.5% from xylose fermentation [1].

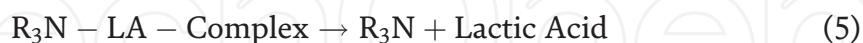


The fermentation requires a stringent control of temperature at 35–45°C and pH of 5–6.5 [34], where the lactic acid production itself can drop the pH, which will have an inhibitory effect on the metabolic activities of the strains [35]. Appropriate bases and salts are added to neutralize the lactic acid to reduce the undesirable consequences of lactic acid accumulation in the industrial operations [3, 35]. The neutralization of lactic acid during fermentation has significant drawbacks, because it necessitates additional steps to recover the undissociated lactic acid from its respective salt so as to use the neutralizing agent again. Calcium hydroxide, $\text{Ca}(\text{OH})_2$, and sulfuric acid, H_2SO_4 , are commonly used in the fermentation process as a conventional neutralizing agent and in liberating lactic acid from calcium lactate, as shown in Eqs. (2) and (3), respectively [1].



Another lactic acid production processes without the formation of gypsum are either using acid-tolerant strains able to ferment both C_5 and C_6 sugars like *Bacillus coagulans* isolates [30], or using $\text{Mg}(\text{OH})_2$ as neutralizing agent that forms *Mg-Lactate*.

The formed *Mg-Lactate* will react with organic amine that is miscible in water, triethylamine (R_3N), Eq. (4), forming both a $\text{Mg}(\text{OH})_2$ crystal and a *triethylamine-LA complex*, ($\text{R}_3\text{N-LA}$) in a SWAP reactor [36], as depicted in **Figure 5**. The $\text{Mg}(\text{OH})_2$ crystal will be filtered and recycled back to fermentation and the *triethylamine-LA complex* will be thermally decomposed to release LA where triethylamine will be recycled back to the SWAP reactor, Eq. (5).



The low volatility and the presence of nonvolatile impurities and other organic acids in the fermentation broth make the recovery of lactic acid challenging.

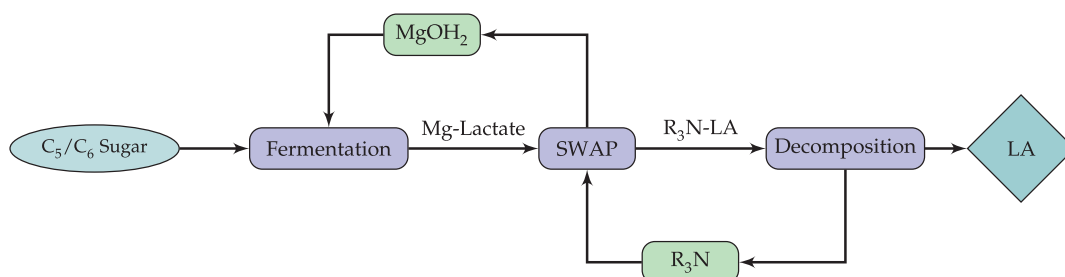


Figure 5. Schematics of the neutralization and recycle of $\text{Mg}(\text{OH})_2$ from the SWAP reactor and R_3N from decomposition of the triethylamine-LA complex. Adopted from a patent, EP1991517B1 [36].

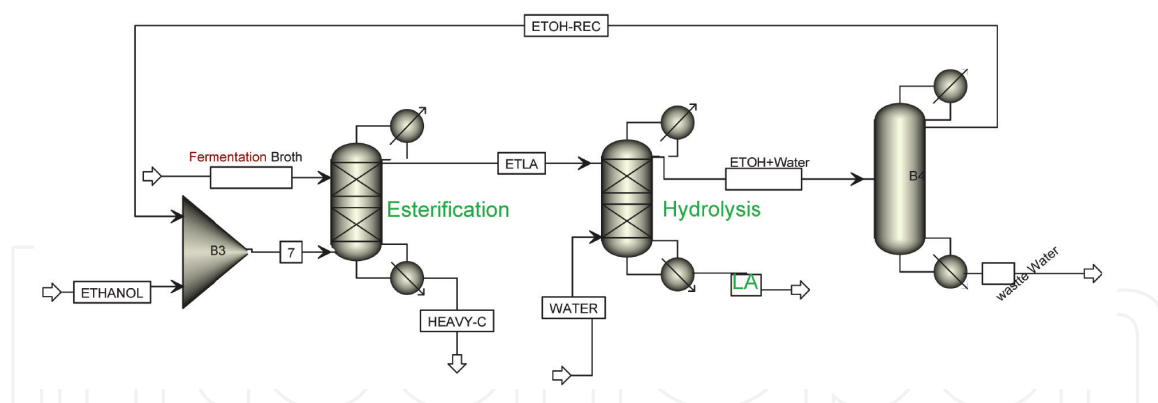
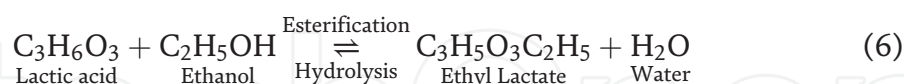


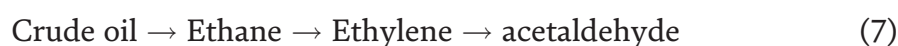
Figure 6. Process flow sheet for the purification of crude LA from the fermentation broth via reactive distillation columns [1].

There are various lactic acid recovery processes from fermentation broth, such as nanofiltration [12, 34], adsorption [37], solvent extraction [38], electrodialysis [39, 40], membrane separation [41], ion-exchange resins [42], and reactive distillation [43, 44]. Reactive distillation [45, 46] was found to be promising at the industrial scale, with some cost advantages [43], and thus, two-step reactive distillation processes are modeled in the present work. Esterification and hydrolysis are the two simultaneous catalyzed reversible reactions that are required for lactic acid recovery by reactive distillation as given in Eq. (6). As shown in **Figure 6**, lactic acid from the fermentation broth is first converted to ethyl lactate (ETLA) in the esterification column using ethanol and this ethyl lactate is then removed from the column by distillation. Pure lactic acid, (99 wt.% L(+)) lactic acid) is then recovered by hydrolysis of the ester (ethyl lactate) with water, in a hydrolysis reactive distillation column. The ethanol that is the top product from the hydrolysis reactive distillation will be purified by normal distillation and recycled (ETOH-REC) to the esterification column [1, 46].



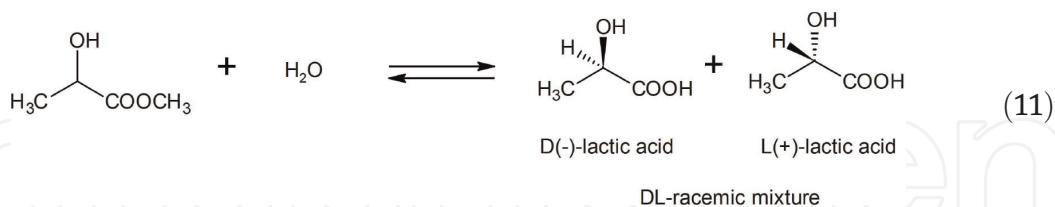
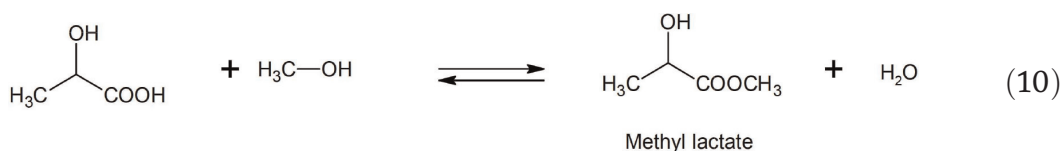
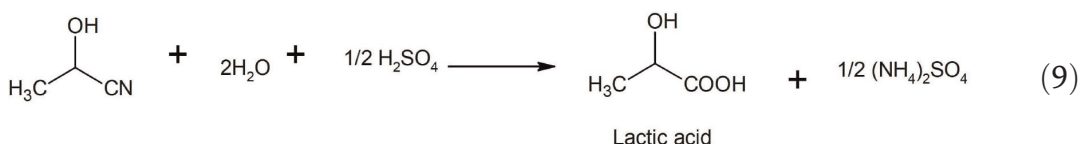
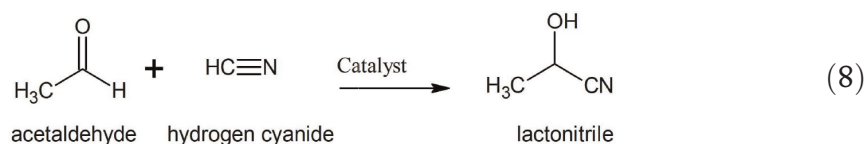
2.4 Lactic acid from non-renewable resources

The commercial process for chemical synthesis is based on lactonitrile [24, 47], $\text{CH}_3\text{CH}(\text{OH})\text{CN}$ as shown in **Figure 2b**. Lactic acid can be chemically produced through various routes, including the conversion of renewable resources and petrochemical-derived materials. One of the commonly used chemical synthesis methods involves the production of lactic acid from acetaldehyde *via* lactonitrile intermediates.



The process begins with the extraction of crude oil, followed by refining to obtain ethane. Ethane is then converted into ethylene through processes such as steam cracking or catalytic cracking. Ethylene is further processed to produce acetaldehyde (CH_3CHO). This can be achieved through the oxidation of ethylene or by direct

hydration of acetylene. Acetaldehyde is a key raw material for the subsequent steps in lactic acid synthesis. Acetaldehyde is reacted with hydrogen cyanide (HCN) in the presence of a base catalyst under high-pressure conditions. This catalytic reaction results in the formation of lactonitrile (acetaldehyde cyanohydrin), Eq. (8) [12]. Lactonitrile is then recovered, purified through distillation, and hydrolyzed using sulfuric acid (H_2SO_4). This hydrolysis reaction converts lactonitrile into lactic acid and ammonium sulfate byproduct as shown in Eq. (9). To further process the lactic acid, Eq. (10) involves esterification with methanol (CH_3OH), leading to the formation of methyl lactate ($\text{CH}_3\text{CHOHCOOCH}_3$). Methyl lactate is subsequently recovered, purified *via* distillation, and hydrolyzed with acidified water in Eq. (11). This hydrolysis step results in the production of lactic acid and the regeneration of methanol. Methanol is separated through distillation and can be recycled for further use. It is important to note that the chemical synthesis route described above typically yields a *racemic* mixture of lactic acid, which consists of equal amounts of D(-)-lactic acid and L(+)-lactic acid. However, in certain applications, such as the production of polylactide, optically pure L(+)-lactic acid is often preferred.



3. Environmental impact assessment

The environmental impact assessment of lactic acid production from various biobased feedstocks have been studied and the environmental benefits compared with fossil-based lactic acid production [1, 48, 49]. Environmental assessment was made using the standard Life Cycle Assessment for determining the potential environmental impacts of biobased lactic acid production processes. Environmental life cycle assessment, a standardized methodology [50], considers the full life cycle of the analyzed biochemical production systems and a broad range of environmental impact indicators, as shown in **Table 1**. A *cradle-to-gate* life cycle assessment is applied considering all steps across production systems, feedstock production, and lactic acid production

Description	Symbol
Abiotic depletion potential measured in kg of <i>substance</i> eq.	ADP
Acidification potential measured in kg of SO ₂ eq.	AP
Freshwater eutrophication potential measured in kg of PO ₄ ⁻³ eq.	FWEP
Marine eutrophication potential measured in kg NO ₃ ⁻ eq.	MEP
Global warming potential measured in kg of CO ₂ eq.	GWP
Ozone layer depletion potential measured in kg of CFC-11 eq. (chlorofluorocarbon)	ODP
Human toxicity potential measured in kg of 1,4-DB eq. (DB:dichlorobenzene)	HTP
Fresh water aquatic ecotoxicity potential measured in kg of 1,4-DB eq	FWAETP
Marine aquatic ecotoxicity potential measured in kg of 1,4-DB eq.	MAETP
Terrestrial ecotoxicity potential measured in kg of 1,4-DB eq.	TETP
Photochemical oxidation potential measured in kg of C ₂ H ₄ eq.	POCP
Metal depletion potential measured in kg Fe eq.	MDP
Ionizing radiation potential measured in kBq U ₂₃₅ eq.	IRP
Particulate matter formation potential measured in kg PM ₁₀ eq.	PM
Water depletion potential measured in m ³ water used	WDP
Agricultural land occupation measured in m ² a	ALO
Urban land occupation measured in m ² a	ULO
Natural land transformation measured in m ²	NLT

Table 1.

Environmental impact categories considered for comparison of biobased lactic acid and fossil based lactic acid production for the LCA study.

as a stand-alone plant or biorefinery processes integrated with existing plants. The potential environmental impacts of a lignocellulosic biomass-based lactic acid process have been investigated by means of a life cycle assessment [50]. A life cycle assessment is carried out for biobased lactic acid from lignocellulosic biomass and compared with fossil-based lactic acid, as described in Sections 2.1 and 2.4, respectively. Similar studies were conducted on comparing environmental impacts of a biodegradable plastic polylactic acid (PLA) compared with fossil based PLA [51–53]. The life cycle assessment complies with ISO [54, 55] standards, as shown in **Figure 7**, consisting of four stages: goal and scope definition, inventory analysis, impact assessment, and interpretation.

Ögmundarson et al. [48] quantified the environmental impacts of biochemical production of lactic acid using different biobased feedstocks like corn, corn stover, and macroalgae (*Laminaria* sp.) and discussed the potential for reducing impact. Despite differences in assumptions and data availability across the *cradle-to-gate* life cycle assessment model for the biobased lactic acid production process, several research works show there is an environmental savings that leads to the global sustainable developments [1, 48, 56]. Replacing fossil-based lactic acid with its biobased lactic acid reduces about 80–99% of the environmental burdens of most of the environmental impact categories [1], making biobased lactic acid is environmentally friendlier than its fossil-based equivalent in most of the impact categories.

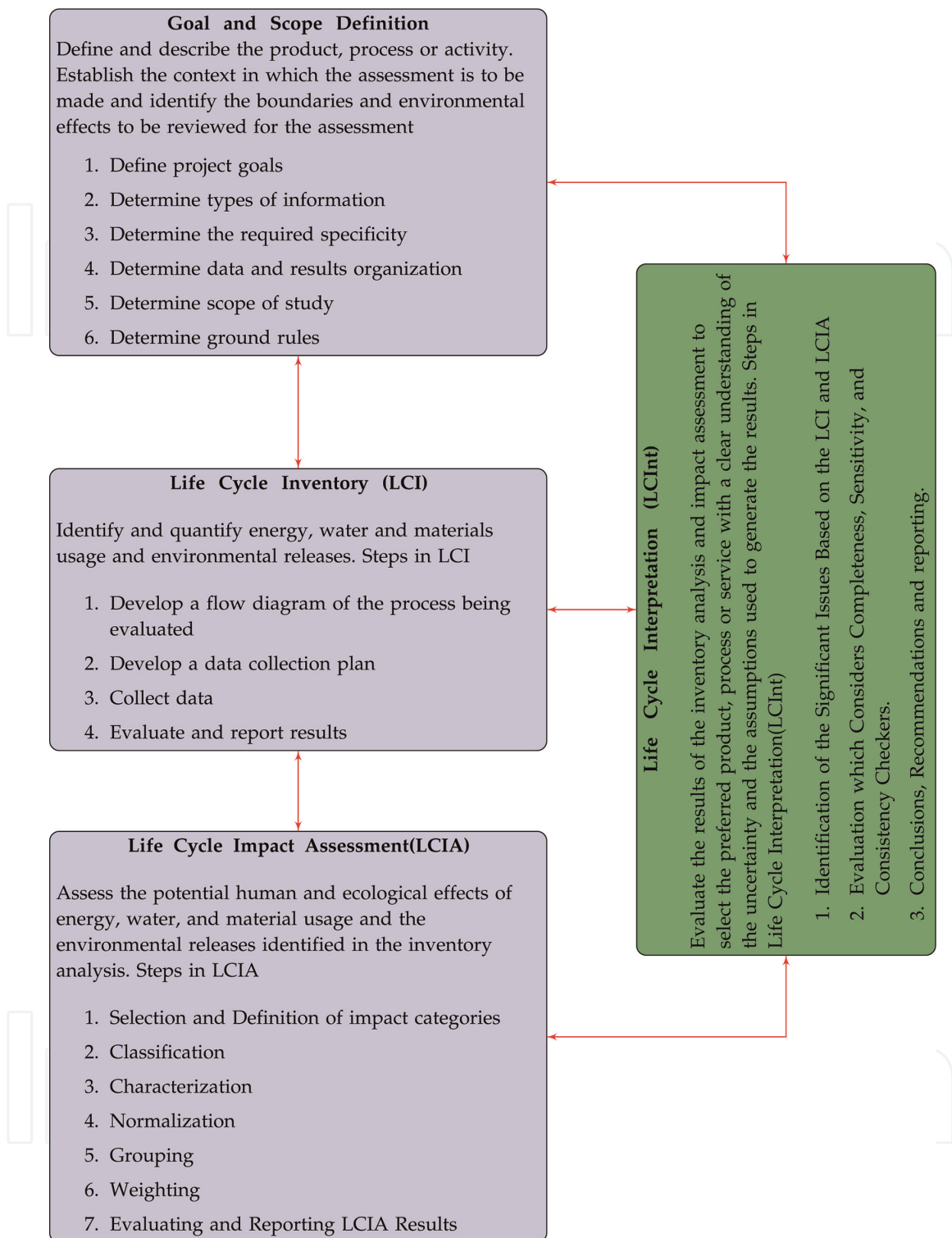


Figure 7. Phases and guidelines of LCA, according to ISO 14040 series.

4. Conclusion

Lactic acid has important applications in various industrial sectors such as the chemical, pharmaceutical, food, and cosmetics industries, where its demand is steadily increasing. Furthermore, lactic acid is an essential building block for numerous commodity and intermediate biobased chemicals like acrylic acid, lactate esters,

1,2-propanediol, pyruvic acid, acetaldehyde, 2,3-pentanedione, ethanedioic acid, and polylactic acid, making it as a suitable alternative to their oil-derived counterparts. The bioconversion processes of converting lignocellulosic biomass into lactic acid need to overcome the following points or challenges: (1) effective pretreatment process to make all C₅ and C₆ sugars available for the selected microorganism that ferment them into stereospecific (L- or D-) lactic acid, (2) selection of suitable microorganism along with their required substrates and fermentation conditions, and (3) employing the separation and purification of lactic acid from the fermentation broth. The promising method for the industrial production of lactic acid will be of continuous simultaneous saccharification and fermentation in a gypsum-free process using Mg(OH)₂ as neutralizer, followed by reactive distillation for purified lactic acid production. The *cradle-to-gate* life cycle assessment model for the biobased lactic acid production process indicated that the about 80–99% of the environmental burdens of most of the environmental impact categories can be reduced compared with its equivalent fossil-based lactic acid, making biobased lactic acid environmentally superior to the fossil-based lactic acid.

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