

Review

Potential Use of Cow Manure for Poly(Lactic Acid) Production

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Abstract: Cow manure is an abundant residue and poses a problem regarding recycling. Intensive animal farming produces manure, which, if not properly managed, can contaminate nearby water bodies and soils with nutrient excess. There are 1.9 billion cattle worldwide, with a calculated capacity to produce 7.6 billion tons per year. Feeding of these cows is carried out mainly with cellulosic material. Therefore, cow manure contains an important fraction of lignocellulose. Cow manure can be valorized using such lignocellulosic fractions as the raw material of several fermentative processes. This fraction can be transformed into sugar, which can, in turn, be used to feed lactic acid bacteria (LAB). LAB produces lactic acid (LA), which can later be polymerized to poly(lactic acid) (PLA), a bioplastic with promising market forecasts. This review describes the most updated processes for all of the necessary steps to produce lactic acid from lignocellulosic biomass with LAB. Key process parameters to obtain PLA from lignocellulose are reviewed and analyzed herein, including lignocellulosic fraction extraction, sugar transformation, pretreatment, hydrolysis, fermentation, purification, and polymerization. This review highlights the potentiality to obtain lignocellulose from cow manure, as well as its use to obtain PLA.

Keywords: bioplastic; lactic acid; PLA; poly(lactic acid); bioeconomy; cellulose; lignocellulose; cow manure; circular economy



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Citation: Garrido, R.; Cabeza, L.F.; Falguera, V.; Pérez Navarro, O. Potential Use of Cow Manure for Poly(Lactic Acid) Production. *Sustainability* **2022**, *14*, 16753. <https://doi.org/10.3390/su142416753>

Academic Editors: Idiano D’Adamo and Massimo Gastaldi

Received: 19 November 2022

Accepted: 10 December 2022

Published: 14 December 2022

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1. Introduction

Synthetic polymers created from fossil fuels have caused significant environmental issues. Current methods of manufacture, use, and disposal are not environmentally friendly and pose risks to both human and animal health. The accumulation of waste in landfills and natural habitats, physical issues for wildlife brought on by ingesting or becoming entangled in plastic, the leaching of chemicals from plastic products, and the possibility that plastics will transfer chemicals to wildlife and humans are just a few of the many issues surrounding their use and disposal [1]. From coastal areas alone, around 20 megatons (Mt) of improperly disposed plastic debris will reach the oceans by 2025 [2], with an additional 1.15–2.41 Mt brought yearly by rivers from inner areas of the planet [3].

One sustainable source of energy and organic carbon for our industrial society is biomass, because it is a renewable resource [4]. Seventy-five percent of the biomass that photosynthesis generates in nature belongs to the class of carbohydrates. Surprisingly, humans only consume 3–4% of these substances for food and non-food uses [5]. It can be used as an alternative to produce biodegradable and/or biobased plastics.

Lignocellulose, as a carbohydrate source, is an attractive raw material for biotechnological operations because of its renewable nature, global distribution, abundance, and low cost. Plant biomass (lignocellulosic biomass) is an abundant, affordable, and ecologically friendly resource that has great potential to be used in the production of fuels and chemicals. Agricultural waste is a good source of lignocellulosic biomass, which is cheap, renewable, and mostly under-utilized. In the past, these resources have included woody

crops, maize stover, sugarcane bagasse, rice hulls, leaves, stems, and stalks from corn fiber. Agricultural and industrial activities generate a variety of types of lignocellulosic waste, such as citrus peel waste, sawdust, paper pulp, industrial trash, municipal solid waste, and paper mill sludge [6]. Cow manure has also a lignocellulosic fraction, which can be used as raw material.

More than 1.4 billion cattle are kept worldwide, and 159 million (11 percent) are in the regions of Europe and Central Asia [7]. Worldwide, Brazil is the country with the most heads [8]. The potential production of cow manure worldwide is 7.6 billion tons per year [9].

The necessity of and opportunity for successful and cost-effective methods that transform lignocellulosic biomass into value-added chemicals, which are now produced from non-renewable resources such as fossil fuels, are highlighted by the abundance of lignocellulosic biomass [1]. Production of LA and PLA from lignocellulosic material has been widely studied.

Chemical synthesis and the fermentation of renewable carbohydrates are both production paths to lactic acid. Using biomass as a carbohydrate source, it is possible to produce LA. LA is an organic acid that occurs naturally and serves as the primary metabolic intermediate in the majority of living bodies, including humans and anaerobic prokaryotes [10]. LA is a versatile organic acid that presents diverse applications, mostly in food and food-related industries. The United States Food and Drug Administration (USFDA) has classed it as Generally Recognized As Safe (GRAS) for general-purpose food additives [11]; it serves a variety of purposes, including flavoring, regulating pH, acting as an acidulant, enhancing microbiological quality, fortifying minerals, and extending shelf life [12]. Ninety percent of LA's worldwide production is achieved through fermentation [13]. Substrates can be renewable and low-cost materials, such as lignocellulosic residues [14]. The production of D-Lactic acid or L-Lactic acid with high optical purity, or a mixture of both with low optical purity, might result from the lactic acid fermentation process, depending on the specific microbe. There are several bacteria that can generate lactic acid, but a competitive commercial process demands a strong, quickly expanding, low-pH, high production strain with affordable nutritional needs. The usual anaerobic fermentation process for *Lactobacillus* uses little energy to run, with the majority of the expense typically coming from medium components such as carbohydrates.

The most widespread biodegradable and biocompatible polymers used today, PLA and poly(lactic-co-glycolic acid) (PLGA), are synthesized and processed using LA [15]. Because of its excellent processing capabilities and strong mechanical characteristics, PLA is one of the most commercially successful bioplastics (at least among the stiff types). Through fermentation, its monomer, lactic acid, is produced from renewable resources such as starch or sugar. After fermentation, lactic acid must be extracted from the broth and purified to the desired requirements in order to produce PLA [16]. The majority of PLA production procedures use ring-opening polymerization (ROP), which is more effectively used to convert lactide (the cyclic dimer of lactic acid) to PLA [17].

PLA is biodegradable and resembles polypropylene (PP), polyethylene (PE), or polystyrene (PS) in terms of its properties. It can be manufactured using currently-in-use manufacturing machinery (those designed and originally used for petrochemical industry plastics). As a result, production is quite inexpensive. In light of this, PLA has the second-highest volume of manufacture of any bioplastic (the most common typically cited as thermoplastic starch). It can be easily converted into molded components, film, or fibers using normal plastic processing machinery [18].

Traditionally, manure waste is used as a fertilizer for agricultural soils or to produce biogas. While biogas is a mixture of methane, CO₂, and other gases, produced by anaerobic digestion of organic materials in an oxygen-free environment, biomethane is a nearly pure source of methane created either by upgrading biogas or by gasifying solid biomass, followed by methanation [19]. However, increasing limitations on its use as a fertilizer [20] or biogas air pollution [21] are key deciding factors.

As stated in [19], data show how much potential for economic growth is being missed by not utilizing renewable sources. The dilemma of having accessible substrates but not using them to create products (or energy) seems to exist. Cow manure lignocellulosic fraction has the potential to be converted into valuable products, falling into the circular bioeconomy field. This paper reviews the most up-to-date knowledge on the unit operations of the process of converting cow manure to PLA, such as the conversion of lignocellulosic material into sugar and its conversion to LA and PLA. To obtain a complete picture of the state of the art, processes from other, extensively researched lignocellulosic material sources are also explored.

2. Cow Manure Composition

Cow manure is an important residue, and that produced in the greatest quantity in rural farms. As a fertilizer, it is suitable for all plants and soils; it gives consistency to sandy and mobile soil and lightness to chalky soil, and also refreshes warm, limestone, and loamy soils. Of all manures, it lasts the longest and is the most uniform. The duration of its strength depends mainly on the kind of feed given to the cattle that produce it.

Production of animal waste worldwide is not counted exactly, but estimations are made based on census and the type of management. Dejection information varies with the species and size of the animal as well as the type of installation, which also has a great influence on the amount and type of waste generated (solid manure or slurry). The European Union (27) generates 1500 million tons of manure annually, mainly from cattle and swine [22]. In Europe, the proportion of the liquid form of the manure (slurry) varies greatly in different countries, from 95% of total production in the Netherlands to 20% in Eastern European countries [23]. Overall, in central Europe, Spain and Portugal, over 65% of the dejections are produced as slurry, with the highest proportion in pig farming [24]. The estimation of Spanish livestock sector's waste production is around 140 million tons per year [25].

The biodegradable fraction is also made up of more complex compounds of slower degradation, such as lipids and relatively stable lignins and tannins, as well as a series of phenolic polymers called melanin, synthesized mainly by fungi, which are characterized by their great similarity to humic acids in terms of composition, structure, and resistance to degradation [26]. In Figure 1, a description of the solid organic fraction transformation is shown.

Livestock manure is classified according to the percentage of dry matter in a solid. Dejections that have approximately more than 20% are characterized as dry matter; those dejections that have around 10–22% dry matter are considered semisolid; and those dejections that have a dry matter content of around 0–15% are liquid or semi-liquid.

The typical composition of both solid and liquid manure is difficult to establish, as it depends on many factors. The fertilizer value of both solid manure and slurry varies greatly from one farm to another, since it depends on the type of farm (breed, species, age, etc.), diet, type of production, type of accommodation, and how the waste is stored. As an example, Table 1 shows the typical nutrient content of manure and slurry studied by different authors.

A cow will consume between 4 and 5 tons of fodder annually on a dry matter basis. Cows are fed a diet that is heavy in lignocellulosic fiber, and following digestion, they generate manure [27]. The most prevalent type of agricultural waste is cow manure, which is also a typical lignocellulosic material [28]. Table 2 shows the dejections produced in a year by a cow.

Cow manure's potential has not yet been fully revealed, because only a small portion of the lignocellulosic fraction has been utilized by microorganisms to produce biogas, leaving huge amounts of the anaerobically digested cow manure unused [29]. Enzymatic hydrolysis into fermentable sugars could effectively disrupt the treated lignocellulosic fraction [30].

Table 3 illustrates the fiber content of the most commonly used cow manure residue. Despite comparing the same type of manure, recorded data display a wide range. This is because different regions of the world have variable levels of animal digestibility, which causes the percentages of lignocellulosic material to vary greatly [31].

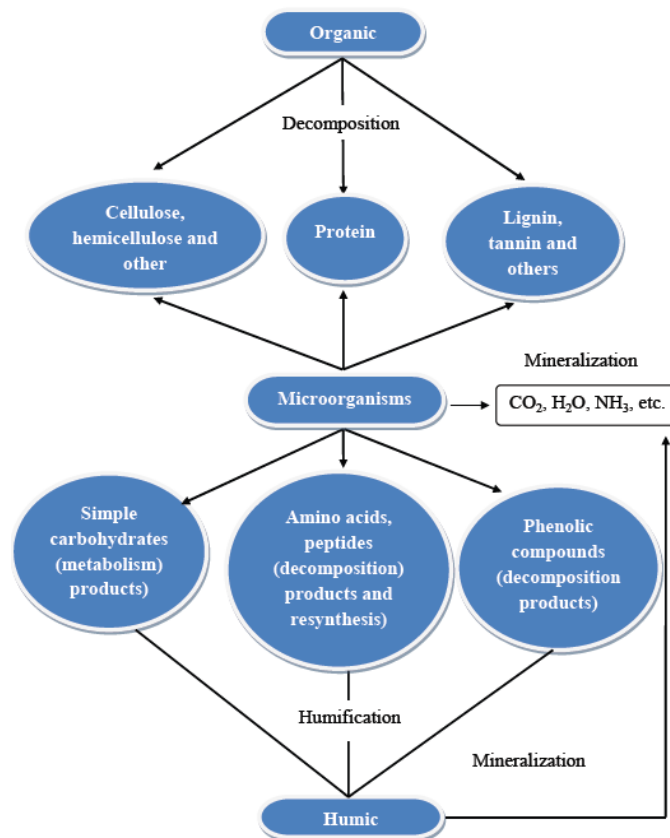


Figure 1. Transformation and evolution of the soil organic fraction. Adapted from [32].

Table 1. General manure composition (g/kg over fresh weight). Adapted from [33].

	Dry Matter		Total Nitrogen		N-Ammonia		Phosphorous	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Liquid manure/slurry								
Cow	65	15–123	3.9	2.0–7.2	2.3	1.0–4.9	2.3	0.2–6.0
Solid manure								
Cow	223	160–430	4.8	2.0–7.7	1.3	0.5–2.5	3	1.0–3.9

Table 2. Characteristics of four typical livestock farms, and the manure they generate. Adapted from [9].

Parameter	Farm A	Farm B
Type of farm	Fattening Cow	Dairy cow
Capacity (places)	850	400
Cycles/year	1.22	1
Produced dejections (ton/year)	1700	8525
Dejections	Stable/manure heap	Pit/Pond
Nitrogen concentration (kg N/ton)	11	4.8

Table 3. Cow manure’s lignocellulosic material percentages.

Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
21.2	30.4	11.6	[34]
23.5	12.8	8.0	[31]
17.9	15.7	18.2	[35]
22.9	22.9	8.1	[36]
26.59	11.27	11.24	[37]
23.51	12.82	7.95	[38]
21.89	12.47	13.91	[39]

The compositions of lignocellulose in cow manure and anaerobically digested cow manure have been examined [40], and the composition data for cow manure are presented in Table 4. The analysis revealed that glucan (16.62%) and xylan (15.26%) formed the majority of cow manure. Different feedstock types and seasonality may have a small influence on the overall conversion process design [41]. Due to the lignocellulose fraction’s breakdown during biogas generation in the anaerobic reactor, the amount of glucan still present in the anaerobically digested cow manure after biogas production was considerably lower than that in the unfermented cow manure. Thus, glucan (14.50%) and xylan (12.56%) were present in anaerobically digested cow manure. These findings showed that cow manure had a relatively high lignocellulosic content, and that the amount of fiber was somewhat reduced during anaerobic digestion for methane generation.

Table 4. Composition of cow manure and anaerobically digested cow manure [40].

Biomass Components	Cellulose (%)	Hemicellulose (%)
Cow manure	16.62	15.26
Alkali-treated cow manure	35.34	15.48
Acid-treated cow manure	26.62	7.61
Anaerobically digested cow manure	14.5	12.56
Alkali-treated anaerobically digested cow manure	28.94	15.98
Acid-treated anaerobically digested cow manure	22.56	3.22

3. Sugar Production from the Lignocellulosic Portion of Cow Manure

A potentially sustainable method of creating innovative bioprocesses and products is through the biotechnological conversion of lignocellulosic biomass. Due to the lignin-protected, highly crystalline structure of lignocelluloses, which is complicated in structure, this substance has a high degree of recalcitrance, making the process of depolymerization a challenge [1].

Enzymatic hydrolysis could be used to successfully transform cow manure into fermentable sugars [42]. It consists of the partition of cellulose into glucose units and the hemicellulosic fraction in their constituent sugars.

While phenolic monomers can be employed as a chemical intermediary in the chemical industry, sugars in cellulose and hemicellulose are attractive as feedstock for fermentation operations [43]. In addition, lignin can be pyrolyzed to provide an oil fuel that can power combustion engines [44].

The majority of pretreatment techniques combine enzymatic hydrolysis with a thermo-chemical process. Thermo-chemical pretreatment can dissolve or deconstruct (part of) the lignin, deacetylate the hemicellulose to increase accessibility, and/or increase the accessibility of cellulose and hemicellulose polymers. By maximizing process variables, including temperature, pressure, pH, and chemical addition, efficient degradation of lignocellulose during chemical pretreatment is possible [42].

In order to use lignocellulosic biomass for value-added product production from its constituent fractions, such as cellulose and hemicelluloses, barriers that prevent chemical or biological catalysts from contributing to its transformation must first be removed. Recalcitrance or alteration of the crystalline structures of the fraction of interest must also be reduced in order to achieve a higher reaction speed and better product quality. It is also preferred that carbohydrates not be broken down, or that no additional products are developed which could stop enzymes or microbes from fermenting. While physical pretreatment refers to size reduction and steam explosion, in chemical pretreatments, biomass structure is altered with solvents that promote cellulose degradation, hemicellulose, and lignin [45].

Most of the lignocellulose must be hydrolyzed twice to become dextrose, a fermentable sugar, utilizing amylolytic enzymes such as α -amylase and glucoamylase. Usually, the first stage is completed quickly at high temperatures (between 90 and 130 °C), then a longer saccharification to dextrose process is completed at cooler temperatures. This technology has been practiced on the industrial scale for decades. Enzymes for this process are highly developed and efficient, and are available at a relatively low cost from companies specializing in industrial enzymes, such as Novozymes and Genencor. The resulting dextrose from this process can then be used for lactic acid fermentation [46]. Figure 2 presents a representation of the lignocellulosic structure, before and after pretreatment.

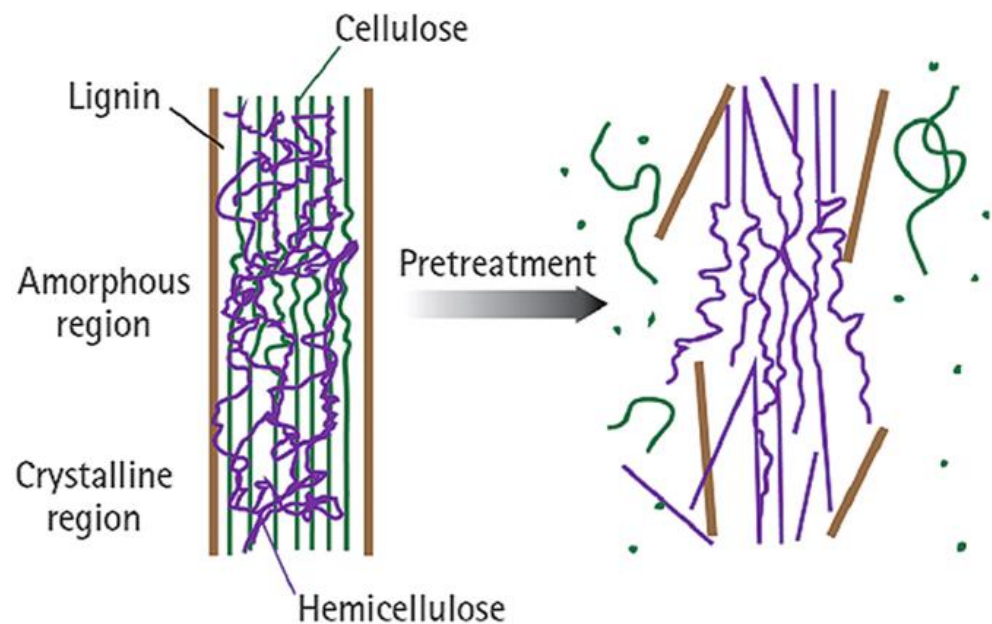


Figure 2. Lignocellulose material structure before and after pretreatment. Adapted from [47].

3.1. Pretreatment

To convert lignocellulosic hemicellulose and cellulose fraction into value-added products, first the elimination of barriers which make accessing its catalysts difficult (biological or chemical) is required. The main purpose of the pretreatment process is to increase the porosity, lower the quantity of crystalline cellulose, and remove lignin and hemicelluloses [37]. Related through the use of physical, chemical, physicochemical, and biological procedures, we can classify different types of pretreatment processes [48]. Figure 3 presents the classification of pretreatments according to their nature.

In terms of byproduct formation, the most critical pretreatments are the chemical ones. Depending on the decomposition method or the lignocellulosic source, different byproducts could be formed. There are three groups of byproducts, namely phenolics, furans, and organic acids [49].

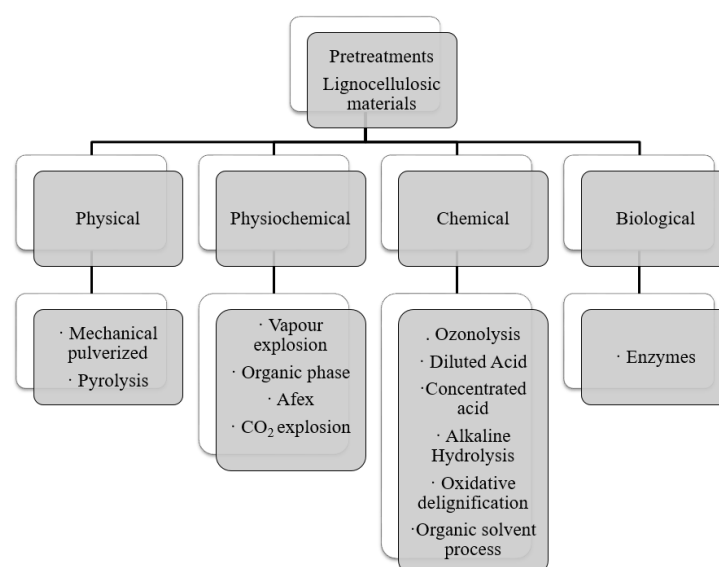


Figure 3. Pretreatment process for lignocellulosic material. Adapted from [45].

3.2. Hydrolysis

An important step is the cellulose partition into glucose units and the hemicellulosic fraction in their constituent sugars. Among several processes for this purpose, two are best-known: acid hydrolysis and enzymatic hydrolysis [50].

3.2.1. Acid Hydrolysis

The acid hydrolysis of polysaccharides comprises the processes in which acid is added at the beginning of the process (acid hydrolysis) and those in which acid is generated during the process (hydrothermal or autohydrolytic). These procedures have the same chemical principle, but differ in their operating conditions, mainly in temperature and acid concentration. The acid hydrolysis processes are mainly classified into concentrated processes and diluted processes. Table 5 presents the pros and cons of this procedure.

Table 5. Advantages and disadvantages of acid hydrolysis. Adapted from [51].

Type of Acid Hydrolysis	Advantages	Disadvantages
Concentrated acid process	Low temperature operation; high sugar performance.	High acid consumption; high energetic cost; long reaction time (2–6 h).
Diluted acid process	Low acid consumption; lower permanence time.	High temperatures; low sugar performance; equipment corrosion; formation of non-desired products (degradation).

Among the chemical pretreatment techniques, dilute-acid hydrolysis is perhaps the most frequently used. It can be used either to prepare lignocellulose for enzymatic hydrolysis or to carry out the actual hydrolysis process, yielding fermentable sugars. In order to pretreat or hydrolyze lignocellulosic materials using dilute-acid procedures, many reactor designs, including batch, percolation, plug flow, countercurrent, and shrinking-bed reactors, have been used. Recent reviews have examined these procedures, as well as many facets of dilute-acid hydrolysis and pretreatment [51,52]. The dilute-acid treatment can achieve high reaction rates and greatly enhance cellulose hydrolysis at high temperatures (e.g., 140–190 °C) and low acid concentrations (e.g., 0.1–1% sulfuric acid). By using diluted acid as a pretreatment, hemicellulose can be removed almost completely. Although the pretreatment does not effectively dissolve lignin, it can disrupt it and make cellulose more accessible to enzymatic hydrolysis [53].

High contents of lignin and glucose have an important inhibitory response to the activity of the enzymatic cocktail, with the final glucose yield decreasing as the addition of the initial concentration of these compounds increases. Other inhibitory compounds (cellobiose, xylose, arabinose, furfural, hydromethylfurfural, and acetic acid) only have a slight effect on cellulose-to-glucose enzymatic conversion, at least at the concentration levels studied. However, it is likely that the synergistic effect of mixtures of these compounds could have a significant negative impact on enzymatic saccharification [54].

Yan et al. [40] studied lignocellulose extracted from cow manure. Cow manure and samples of anaerobically digested cow manure were milled using a micromiller prior to material processing, and they were then thoroughly dried at 45 °C. A one-gram sample was pretreated with 10 milliliters of either 2% sulfuric acid or 2% sodium hydroxide (m/v) in a 500-milliliter conical flask. The lignocellulosic fraction was extracted by two methods. (i) Treated with NaOH: The surface area of the air-dried cow manure materials was increased physically by milling, and the resistant structure was then disrupted by soaking the cow manure in an alkaline NaOH solution. Then, a further detoxification procedure, including water washing, was carried out to remove any remaining chemicals that prevented further microbial fermentation. (ii) Treated with H₂SO₄: lignin and hemicelluloses were further removed during the dilute-acid pretreatment of biomass materials, which enhanced the enzymatic hydrolysis of the biomass to cellulose [55].

3.2.2. Enzymatic Hydrolysis

Several authors have presented theories to explain the total degradation of cellulose. These involve the three enzymatic components of cellulase and the synergism between these, where endoglucanases attack to the amorphous regions of cellulose fibers, creating sites for exoglucanases that would be directed towards the crystalline fiber region. The β -glucosidases would execute the last step of the hydrolysis and would prevent the accumulation of cellobiose, which would inhibit exoglucanases [56].

Other authors have suggested cellulose degradation according to the following steps: (i) adsorption and formation of the substrate enzyme complex; (ii) formation of the product; and (iii) desorption and re-adsorption of the enzyme, or movement of the enzyme along the cellulose molecule. On a string cellulose model, extended hydrolysis of the outer chains would expose the non-terminal internal chain reducers.

The performance of the enzymatic hydrolysis stage depends on the pretreatment used. Alkaline and acid pretreatment methods present performances of less than 85% after hydrolyzing with enzymes, contrary to pretreatments where only water is used in its explosion forms, steam and hot liquid water [57], where performance exceeds 90%. Table 6 summarizes process yields for different types of biomass.

Table 6. Process yields summary for different biomasses [45].

Raw Material	Pretreatment	Enzymes	Hydrolysis Conditions	%	Reference
Corn bran	AFEX	Specyme Cp Accellerase 1000	T = 50, t = 48 h, 15 mg/g glucose	40%	[41]
Cassava bagasse	—	Termamyl 120 L AMG 200 L	T = 90 °C, t = 1 h, pH = 6.5 T = 60 °C, t = 24 h, pH = 4.5 T = 50 °C, t = 96 h, pH = 4.8	97.3%	[58]
Palm oil logs	AFEX	Accellerase 1000	N = 170 rpm	95.4%	[59]
Corn		Celluclast 1.5 L Novozyme 188	T = 50 °C, t = 72h, N = 150 rpm, pH = 5	80%	[60]
Cane bagasse	Diluted organosolv acid	Celluclast 1.5 L Novozyme 188 Xilanasa	T = 50 °C, t = 24 h, pH = 4.8 N = 150 rpm	48–76%	[61]
Cane bagasse	Diluted phosphoric acid	Biocellulase W Novozyme-188	T = 50 °C, t = 96 h, pH = 5 N = 100rpm	74%	[62]
Banana tree	Gelatinization	Celluclast 1.5 L Novozyme-188 Pectinasa (P-2611)	T = 50 °C, t = 9 h, pH = 5	80%	[63]

For acid-pretreated corn stover (PCS), the outcome of fluid dynamic parameters on enzymatic hydrolysis was assessed. When enzymatic PCS biomass saccharification is carried out in a stirred tank batch reactor, with low rotating speeds (<100 rpm) and final Reynolds number (Re) values (<10), a low glucose yield is obtained, with no effect due to higher amounts of enzymes. With stirring speeds over 300 rpm (final Re > 2000), maximal and similar glucose yields are retrieved. Estimated mass transfer coefficients and rates increase with agitation and reaction time. Low stirring speed involves overall rate control by mass transfer, while higher values rapidly lead to low viscosity, high Re, and enhanced mass transfer, with enzymatic reactions as the overall process-controlling step [64].

4. Microbial Fermented Lactic Acid Production

The common term for 2-hydroxypropanoic acid is lactic acid. L(+)-lactic acid and D(-)-lactic acid are the two optical isomers of lactic acid. D(-)-lactic acid can occasionally be hazardous to human metabolism, and can cause acidosis and decalcification [11].

Chemical synthesis and microbiological fermentation can both produce lactic acid. The biotechnological approach for producing lactic acid has various benefits over chemical synthesis, including lower substrate prices, lower production temperatures, and less energy usage [10].

Lactic acid fermentation and product recovery and/or purification are typically included in biotechnological methods for lactic acid production. Numerous studies have been conducted on the creation of biotechnological techniques for the production of lactic acid, with the ultimate goal being to make the process more effective and affordable [12].

From agricultural waste, byproducts, and residues, LA can be synthesized biotechnologically and used to create biodegradable, biocompatible LA polymers. It can also be made from the lignocellulosic component of cow manure, and then turned into sugars which feed LAB. These polymers are often utilized in high-end applications, but with lower production costs, they could find use in a far wider range of applications [65].

The primary method for creating LA is based on the fermentation of various raw materials by microorganisms that produce it, such as bacteria, fungi, and yeast [66]. Group of wild LA producers includes bacteria (LAB: *Carnobacterium*, *Enterococcus*, *Lactobacillus*, *Lactococcus*, *Leuconostoc*, *Pediococcus*, *Streptococcus*, *Tetragenococcus*, *Vagococcus*, and members of the genus *Bacillus*) and fungi (several species belonging to the genera *Mucor*, *Monilia*, and *Rhizopus*) [65].

Microorganisms can be either homofermentative or heterofermentative. Homofermentative LAB use the Embden–Meyerhof–Parnas (EMP) route to convert 1 mol of glucose into 2 mol of LA. Depending on the available substrates, ambient factors, etc., heterofermentative LAB can use either the EMP or phosphoketolase (PKP) route, with the end products being a mixture of LA, ethanol, acetate, and CO₂, or even mannitol in the case of fructose catabolism [66,67].

The majority of the world's commercially manufactured lactic acid is created by using homolactic organisms from the genus *Lactobacillus*, which only produce lactic acid. The following organisms are the main producers of the L(+)-isomer: *Lactobacillus amylophilus*, *L. bavaricus*, *L. casei*, *L. maltaromicus*, and *L. salivarius*. Strains such as *L. delbrueckii*, *L. jensenii*, or *L. acidophilus* produce either the D-isomer or mixtures of both. Under typical fermentation conditions, such as relatively low to neutral pH, temperatures around 40 °C, and low oxygen concentrations, these strains exhibit significant carbon conversions from feedstock [1]. Among the members of the genus *Lactobacillus*, *Lactobacillus Casei* has frequently appeared in studies on the generation of lactic acid [68].

Depending on the source of the lignocellulosic material, the liquid phase produced by hydrolyzing cellulose and hemicellulose contains six-carbon sugars (hexoses) and five-carbon sugars (pentoses). The syrup will primarily contain glucose, xylose, arabinose, galactose, mannose, and rhamnose [69].

The optimal settings for the lactic acid formation route including bacteria (*Lactobacillus* sp.) are pH between 5–7, temperature between 40–45 °C [70–75], a nutrient-rich environ-

ment, and sterile conditions. To maintain the pH, the lactic acid created during fermentation must be neutralized, which increases the cost of lactic acid production and recovery. Using fungi, lactic acid fermentation is another option (*Rhizopus* sp.). Compared to bacteria, fungi can grow in nutrient-limited conditions and efficiently ferment both hexose and pentose carbohydrates [76]. However, because other products (such ethanol and fumaric acid) are produced during fungal fermentation, the amount of lactic acid obtained is reduced [77]. Aeration is also necessary during the fungal fermentation process for larger lactic acid yields, which raises the price of lactic acid production. Yeast can also be used to make lactic acid, and because it can ferment at low pH levels, there is no longer a need to neutralize and recover lactic acid [46]. An overview of the performance of different processes studied for LAB can be found in Table 7.

Table 7. Microorganism productivity for LA.

Organism	Substrate	Lactic Acid Production [g/L]	Yield [g/g]	Productivity [g/(L·h)]	Reference
<i>Enterococcus faecalis</i> RKY1	Glucose	144	0.96	5.1	[78]
	Molasses	95.7	0.95	4.0	[79]
	Corn starch, potato, and wheat	129.9	1.04	1.5	[80]
	Wood hydrolyzate	93	0.93	1.7	[81]
<i>E. mundtii</i> QU 25	Modified Rogosa and Sharpe (mMRS)	119	0.83	1.12	[82]
	Xylose	86.7	0.84	0.9	[83,84]
<i>Lactobacillus rhamnosus</i> ATCC 10863	Biomass pellets and glucose	67	0.84	2.5	[85]
<i>Lactobacillus rhamnosus</i> ATCC 7469	Paper sludge	73	0.97	2.9	[86]
<i>Lactobacillus rhamnosus</i> CECT-288	Yeast and meat extract, peptone	32.5	0.88	5.4	[87]
	Cellulosic biosludges	42	0.38	0.87	[88]
<i>L. casei</i> subsprhamnosus	Softwood	21.1–23.75	0.74–0.83	0.15–0.23	[89]
<i>L. rhamnosus</i> and <i>L. brevis</i>	Cornstover	20.95	0.7	0.58	[90]
<i>Lactobacillus rhamnosus</i> strain CASL	Cassava powder	175.4	0.71	1.8	[91]
<i>L. rhamnosus</i> ATCC 7469	Distillery stillage	97.1	–	1.80	[92]
<i>L. rhamnosus</i> ATCC 7469	Malting, brewing, and oil production byproducts	58.01	–	1.19	[93]
<i>Lactobacillus helveticus</i> ATCC 15009	Whey permeate and yeast extract	65.5	0.66	2.7	[94]
<i>Lactobacillus bulgaricus</i> NRRL B-548	Lactose, glucose, and galactose	38.7	0.9	3.5	[95]
<i>L. bulgaricus</i> CGMCC 1.6970	Dairy waste	113.18	–	2.36	[96]
<i>Lactobacillus casei</i> NRRL B-441	Barley malt sprouts	82	0.91	5.6	[97]
<i>E. casseli flavus</i> and <i>L. casei</i>	Xylose and glucose by co-cultivation	95	–	–	[98]
<i>L. casei</i> NCIMB 3254	Cassava bagasse	83.8	0.96	1.4	[99]
<i>L. casei</i> and <i>L. lactis</i>	Date juice extract	60.3	–	3.2	[100]
<i>L. casei</i> ATCC 10863	Ram horn waste	–	0.08	–	[101]

Table 7. Cont.

Organism	Substrate	Lactic Acid Production [g/L]	Yield [g/g]	Productivity [g/(L·h)]	Reference
<i>L. casei</i> TISTR 390	Sugarcane bagasse	21.3	–	0.18	[102]
<i>Lactobacillus pentosus</i> ATCC 8041	Trimmings of vine shoots	21.8	0.77	0.8	[103]
<i>L. pentosus</i> CECT-4023T (ATCC-8041)	Corn cobs	24	0.76	0.51	[104]
<i>L. brevis</i> and <i>L. pentosus</i>	Wheat straw	7.1	0.95	–	[105]
<i>L. pentosus</i>	<i>L. pentosus</i>	74.8	0.65	–	[106]
<i>Lactobacillus amylophilus</i> GV6	Wheat flour	76.2	0.7	0.8	[107]
<i>Bacillus sp. strain</i>	Corn cob molasses	74.5	0.5	0.38	[14]
<i>Bacillus coagulans</i> strains 36D1	Paper sludge	92	0.77	0.96	[70]
<i>Bacillus coagulans</i> DSM 2314	Lime-treated straw	40.7	0.43	–	[71]
	Sugarcane bagasse	58.7	0.73	1.81	[72]
<i>B. coagulans</i> IPE22	Lignocellulosic hydrolysates	50.48	–	3.16	[73]
<i>B. coagulans</i>	Coffee pulp hydrolysate	48.0	–	1.20	[74]
<i>Lactobacillus sp.</i> RKY2	Glucose, corn steep liquor, and yeast extract	27	0.9	6.7	[108]
	Amylase-treated rice and wheat brans	129	0.95	2.9	[109]
<i>Lactobacillus bif fermentans</i> DSM 20003	Wheat bran syrup	62.8	0.83	1.2	[110]
<i>L. lactis</i> RM2-24	α -cellulose	73	0.73	1.52	[111]
	Molasses and cellbiose	70	0.88	1.45	[112]
<i>Lactococcus lactis</i> IO-1	Sugarcane bagasse	10.9	0.36	0.17	[113]
<i>Lactococcus lactis sp. lactis</i> IFO 12007	Raw cassava starch	90	0.76	1.6	[114]
<i>Lc. Lactis</i> IO-1	Yeast extract, polypeptone, and xylose	33.26	0.68	–	[115]
<i>L. lactis</i> sub sp. lactis AS211	Wheat flour	–	0.77	–	[116]
<i>L. lactis</i> sub sp. lactis ATCC 19435	Wheat starch	–	–	1.5	[117]
<i>Sporolactobacillus sp.</i> CASD	Peanut meal	207	0.93	3.8	[118]
<i>Sporolactobacillus laevolacticus</i> DSM442	Agricultural waste cottonseed	144.4	–	4.13	[119]
<i>L. brevis</i>	Hydrolysate of lignocellulosic	39.1	0.7	0.81	[120]
<i>L. coryniformis</i> ATCC 25600	Yeast and meat extract	54	0.89	0.5	[121]
<i>L. coryniformis</i> spp. Torquens ATCC 25600	Waste cardboard	23.4	0.56	0.48	[122]
<i>Lactobacillus coryniformis</i> ATCC 25 600	Pretreated cardboard	23	0.56	0.49	[123]
<i>L. coryniformis</i> sub sp. Torquens ATCC 25600	Pulp mill residue	55.7	–	2.80	[124]

Table 7. Cont.

Organism	Substrate	Lactic Acid Production [g/L]	Yield [g/g]	Productivity [g/(L·h)]	Reference
<i>Lactobacillus plantarum</i> ATCC 21028	Lactobacilli Man–Rogosa–Sharpe (MRS) broth (ATCC formula 416, DIFCO 0881)	41	0.97	1	[125]
<i>L. plantarum</i>	Alfalfa fiber	46.4	0.46	0.64	[126]
<i>L. plantarum</i> (Recombinant)	Celooligosaccharides and β -glucan	1.47	–	–	[127]
	Arabinose	38.6	0.82	3.78	[128]
	Xylose	41.2	0.89	1.6	[129]
<i>Leuconostoc lactis</i> SHO-47 and SHO-54	Xylo-oligosaccharide	2.3	–	–	[130]
<i>Bacillus</i> sp. Strain 36D1	Solka floc	40	0.65	0.22	[131]
<i>L. salivarius</i> NRRL B-1950	Soy molasses	–	0.76	–	[132]
<i>Lactobacillus</i> sp.	Sugarcane juice	8.1	–	–	[133]
<i>L. amylovorus</i>	Cassava starch substrate	4.8	–	–	[134]
<i>Leuconostoc mesenteroides</i> NRRL B 512	Yeast extract and sugarcane juice	60.2	–	1.25	[135]
Mixed culture of <i>B. coagulans</i> LA1507 and engineered and adapted <i>E. coli</i> WYZ-L	Sweet sorghum juice	118.0	–	1.84	[136]
	Molasses and corn steep liquor	75.0	–	0.48	[137]
<i>Bacillus</i> sp. XZL9	Corn cob molasses	74.7	–	0.38	[14]
<i>L. paracasei</i>	Sweet sorghum	88	0.79	–	[138]
Adapted <i>L. paracasei</i> A-22	Agro-industrial substrate	169.9	–	1.42	[139]
<i>L. paracasei</i> LA104/ <i>L. coryniformis</i> ATCC 25600	Waste Curcuma longa biomass	97.1	–	2.70	[140]
<i>Lactobacillus</i> sp. B2	Crab (<i>Callinectes bellicosus</i>) wastes	19.5	–	0.81	[141]
<i>R. oryzae</i> TS-61	Chicken feather protein hydrolysate and sugar beet molasses	38.5	–	0.92	[142]
<i>R. oryzae</i> NLX-M-1	Xylo-oligosaccharides manufacturing waste residue	60.3	–	1.0	[143]
<i>R. oryzae</i> As 3.819	Tobacco waste extract	173.5	–	1.45	[144]
<i>Delbrueckii</i> IFO 3202	De-fatted rice bran	28	0.78	0.28	[145]
<i>Delbrueckii</i> NCIMB 8130	Molasses	90	0.97	3.8	[146]
<i>Lactobacillus delbrueckii</i> Uc-3	Cellobiose and celotriose	90	0.9	2.3	[147]
<i>L. delbrueckii</i> mutant Uc-3	Molasses	166	0.87	4.2	[79]
	Waste sugarcane bagasse	90	0.9	2.25	[148]
	Molasses	166	0.87	4.2	[79]
<i>Delbrueckii</i>	Sugarcane juice	118	0.95	1.7	[149]
<i>L. delbrueckii</i>	Alfalfa fiber	35.4	0.35	0.75	[126]
<i>L. delbrueckii</i> NRRL-B445	Cellulosic material	65	0.18	–	[150,151]
<i>L. delbrueckii</i> NCIM 2025	Cassava bagasse	81.9	0.94	1.36	[99]
<i>L. delbrueckii</i> UFV H2B20	Brewer's spent grain	35.5	0.99	0.59	[152]

Table 7. Cont.

Organism	Substrate	Lactic Acid Production [g/L]	Yield [g/g]	Productivity [g/(L·h)]	Reference
<i>L. delbrueckii</i> ZU-S2	Cellulosic material	48.7/44.2	0.95/0.92	1.01/5.7	[153]
	Cellbiose and celltriose	90	0.9	2.3	[147]
	α -cellulose	67	0.83	0.93	[148]
<i>Lactobacillus delbrueckii</i> HG 106	Unpolished rice	90	0.73	1.5	[154]
<i>L. delbrueckii</i> sub sp. Lactis	Starch	–	1.0	–	[155]
<i>L. delbrueckii</i> NRRL B-445	Molasses	–	0.81	–	[156]
<i>L. delbrueckii</i> sp. lactis NCDC290/ <i>L. delbrueckii</i> sp. <i>Delbrueckii</i> NBRC3202	Kodo millet (<i>Paspalum scrobiculatum</i>) bran residue	10.53	–	0.44	[157]
Engineered and adapted <i>Pediococcus Acidilactici</i>	Yeast extract, peptone, and glucose	130.8	–	1.82	[158]
<i>S. inulinus</i> YBS1-5	Wheat bran, corn steep liquor, and yeast extract	70.7	–	0.65	[159]

Note: production (g/L): grams of LA produced by liter (biomass concentration). Yield (g/g): product yield per gram of substrate. Productivity (g/L·h): grams of LA produced every hour per liter (biomass concentration).

4.1. Simultaneous Saccharification and Fermentation

By combining the enzymatic hydrolysis of carbohydrate substrates and the microbial fermentation of the produced sugars into a single process, also referred to as “Simultaneous Saccharification And Fermentation” (SSAF), the bioconversion of carbohydrate sources to lactic acid can be made significantly more effective [1]. Due to lactic acid’s low added value as a bulk chemical, it is necessary to convert lignocellulosic material into lactic acid in an effective manner with high productivities and yields [72,160].

Enzymatic hydrolysis should proceed significantly faster when fermentation and enzymatic hydrolysis are coupled in an SSAF process, because the microbe can directly absorb the monomerized sugars, reducing product inhibition. Thus, the processing time of SSAF can be drastically decreased [161]. Moreover, the complete hydrolysis of the carbon substrates before fermentation is not necessary with SSAF. Enzymatic hydrolysis, cell development, and microbial generation all take place concurrently throughout the SSAF process. SSAF’s ability to lessen the inhibition brought on by mono- or disaccharide buildup raises the saccharification rate, which will, in turn, increase productivity and minimize reactor volume and capital costs [1].

To increase process effectiveness, SSAF is combined with dilute acid or hot water pretreatments. Cellulases and xylanases are responsible for converting carbohydrate polymers into fermentable sugars, which are susceptible to inhibition by the products (glucose, xylose, cellobiose, and other oligosaccharides) [162].

There is an important fraction of minor sugars in lignocellulosic biomass. From an economical and production perspective, the ability to ferment minor sugars has to be verified. LAB laboratory testing shows the sugar consumption order of the microorganisms: glucose first, then mannose, followed by xylose and galactose almost at the same time [89].

Some thermophilic *Lactobacilli* can ferment pentoses (arabinose and ribose) homofermentatively [163]. It has also been reported that strains related to *L. salivatrius*, further described as *L. murinus* [164], exhibited the same property.

The yield of *B. coagulans* IPE22 was enhanced with glucose as substrate, but xylose as substrate enhanced cell proliferation. This demonstrated how the characteristics of

simulated mixed sugar would affect the efficiency of LA fermentation, but not necessarily the amount of LA that would be produced in the end [73].

The reduction in end-product inhibition of the enzymatic hydrolysis, as well as the decreased investment costs, are the main advantages of conducting the enzymatic hydrolysis concurrently with the fermentation, rather than in a separate phase. This process has a higher hydrolysis rate, and requires a low enzyme load, higher product yield, lower risk of contamination, shorter time process, and smaller reactor volume. On the other hand, the major disadvantages include the necessity to find optimal conditions (for example, temperature and pH) for both enzymatic hydrolysis and fermentation, as well as the challenge of recycling the fermenting organism and the enzymes. The temperature is typically kept below 37 °C to meet the first condition [165].

Simultaneous Saccharification and Co-Fermentation (SSCF) has been demonstrated to be an efficient bioconversion strategy for LA production. With regard to yield and productivity, fermentation of LA from lignocellulosic feedstock has been investigated extensively [166]. *Lactobacillus pentosus* metabolizes hexose (glucose) through the EMP pathway under anaerobic conditions, producing LA as the sole product (homofermentation). It also ferments pentoses (xylose and arabinose) through the PKP pathway, generating equal mole fractions of LA and acetic acid (heterofermentation) [106].

4.2. Lactic Acid Recovery

LA recovery processes are still not viable for industrial application. The principal disadvantages are equipment costs, solvent recovery, and energy consumption.

The purification and separation of LA involve several processes, which make up 50% of the process cost [167,168]. The principal drawbacks to achieving a high purity LA are due to its decomposition at elevated temperatures, its high energy consumption, and its affinity with water [169]. Table 8 compares different methods available for the separation and recovery of LA from final broth.

Membrane recovery processes are very effective, but their drawbacks include high membrane cost, polarization, and fouling problems. The solvent method requires a high exchange area, and it also has high solvent costs and high toxicity of extractants. There are some promising advances in terms of novel extractants. The precipitation method is the most widely used, but it creates lactic acid with low purity and solid waste residue, and is economically competitive [170].

Table 8. LA separation and recovery methods after SSAF. Adapted from [170–172].

Process	Advantage	Disadvantage	Reference
Precipitation	Can be applied in industrial plants Easy to operate Elevates product yield	Sulfuric acid consumption is high Generation of gypsum, which requires landfill disposal Product purity is low	[170,173–175]
Liquid extraction	Gypsum is not produced Thermal decomposition risk decreased	Regeneration by distillation or back-extraction (stripping) of the extractants is needed Purity is low Disadvantageous distribution coefficients of the extraction agents	[170,175–177]
Membrane processes	Scale of production flexibility High differentiation Good performance at purification Possibly to integrate with current fermenters	High membrane cost Membrane fouling Polarization problems Retention of lactic acid Difficult to increase production	[170,178,179]

Table 8. Cont.

Process	Advantage	Disadvantage	Reference
Molecular distillation	Low thermal decomposition risk High differentiation No solvents needed No need for purification	Difficult to increase production High vacuum needed	[171,179,180]
Reactive distillation	Reaction and separation realized together Elevates purification values Energy consumption is low	Mechanism is complex Reversible chemical reactions in the liquid phase applicability Applications are restricted to systems with reasonably fast reaction rates and no mismatch between the temperatures suitable for reaction and separation Homogeneous catalyst usage could cause corrosion and separation issues	[170]
Ion exchange adsorption	No waste generated Easy and simple to operate Elevate operational stability and selectivity Accelerated product recovery Low maintenance expenses and energy usage Not toxic to microorganisms Possibility to be integrated in an heterogeneous system Reusable resin	Large liquor waste as a result of widespread fluent use Only applicable with low temperatures and short-/mid-term production Co-extraction of other compounds is difficult	[181–188]

4.3. Purification of Lactic Acid

The purification of LA from the fermentation broth is a vital step for its commercialization, since high-purity LA is required as a building block for the synthesis of high value-added products, such as PLA and other chemicals. When both isomers are created during fermentation, the purification stage might become even more challenging, as some applications require optically pure D-Lactic acid or L-Lactic acid [189].

Usually, two methods are used: (i) the crude lactic acid is obtained by acidifying the cleared fermented liquor with sulfuric acid, with a concentration of 32%, which is substantially above the crystallization point; (ii) using the method outlined in [190,191], the crude calcium salt that precipitates from the concentrated fermented liquor is crystallized, filtered, dissolved, and then acidified with sulfuric acid. This method uses filtering and washing to separate the precipitated calcium lactate from the dissolved contaminants. However, certain contaminants are still present in the cake. Along with the washes, calcium lactate is lost. The calcium lactate method is currently the most frequently used strategy for separation. This technique, which is based on calcium hydroxide precipitation, is already being used commercially by NatureWorks and Purac in starch-based LA production methods [177].

The traditional method produces enormous amounts of calcium sulphate cake. It is difficult to eliminate cake that still contains organic pollutants. Filtered fermented broth primarily contains contaminants including color, various organic acids, and remaining sugar compounds [13]. Reactive extraction, adsorption, electrodialysis, and esterification–hydrolysis with distillation are methods for removing these contaminants.

Calcium carbonate is first used to neutralize the fermentation broth using the conventional chemical separation procedure. After filtering the broth containing calcium lactate, in order to remove cells, sulfuric acid is added to acidify it and to create LA and insoluble calcium sulfate [10]. In addition, hydrolysis, esterification, and distillation are used to

produce pure lactic acid. The creation of a significant amount of calcium sulfate (gypsum) as a byproduct, in addition to the high sulfuric acid consumption, are drawbacks of this method [192]. Adsorption [193], reactive distillation [194], ultrafiltration and electro dialysis [10,195–198], and nanofiltration [199,200] have all been investigated as alternative lactic acid separation technologies that do not produce salt waste. Compared to conventional chemical separation methods, these processes are more economical and energy-efficient. Additionally, they have a number of benefits, such as the absence of costly solvents, adsorbents, or energy-intensive phase transitions, as well as the potential for the simultaneous separation and concentration of lactic acid [201].

4.4. Byproduct Formation

The fermentability of substrates obtained from lignocellulose can be negatively impacted by byproducts created during the pretreatment of lignocellulose. The majority of the lignocellulosic byproducts produced can significantly prolong lag phases, reduce productivity, and/or restrict the growth of microorganisms. There are three main categories of lignocellulosic byproducts that can be identified: phenolics, furans, and small organic acids [49].

As a way to deal with the issues caused by byproducts produced during the fermentation of pretreated lignocellulose into LA, three solutions have been presented: (i) It is possible to enhance thermochemical pretreatment techniques to limit the production of byproducts. Since a decrease in byproduct synthesis should not affect the accessibility of hemicellulose to enzymes, achieving this goal can be challenging. Furthermore, since some of the byproducts are inherent to the hemicellulosic structure and are produced during the monomerization of hemicellulosic sugars, their synthesis cannot be completely avoided. Acetic acid, ferulic acid, and coumaric acid are a few examples. The correct pretreatment conditions can considerably limit the formation of additional chemicals that are not a part of the lignocellulose structure, including furfural, without compromising sugar monomerization or accessibility [103]. (ii) After lignocellulose has completed thermochemical pretreatment, byproduct removal can be implemented immediately. Examples include utilizing microbial detoxification, extracting byproducts using active charcoal or lime, or washing pretreated lignocellulose with extremely hot water. Byproduct removal can be an efficient way to limit the number of byproducts in the substrates made from lignocellulose, but this complicates the process, raising costs and perhaps causing a (slight) material loss [202,203]. (iii) Microorganisms can be reinforced to survive greater byproduct concentrations. Methods such as genetic engineering, evolutionary engineering, or mutagenesis can be used to make this improvement. Although the use of genetic engineering and evolutionary engineering may be challenging and time-consuming in some circumstances, and few targets for genetic engineering have been identified, it may be a potent tool to lessen the impact of byproducts on the microorganism.

5. PLA Production by Lactic Acid Polymerization

PLA with variable molecular weight can be produced using LA, although typically only high molecular weight (Mw) PLA has significant economic use in the fiber, textile, plastics, additive manufacturing [204], printed circuit board [205], and packaging industries [206].

The indirect way of obtaining PLA from the lactide, known as ring opening, is the most widely employed technique. It has been shown to be the most efficient method in the industry for producing high molecular weight polymers, and it has the highest implantation. Two of the largest PLA makers use it: Corbion-Purac (Amsterdam, the Netherlands; www.corbion.com, accessed on 7 July 2021) and NatureWorks LLC (Minnetonka, Minnesota; www.natureworkslc.com, accessed on 7 July 2021). Lactic acid is first oligomerized and then depolymerized in the indirect process to create lactide, a cyclic dimer of lactic acid. Following this, ROP transforms lactide into PLA. The three primary techniques for producing high Mw PLA from LA are shown in Figure 4: (1) direct condensation poly-

merization; (2) direct polycondensation in an azeotropic solution; and (3) polymerization through lactide formation [18].

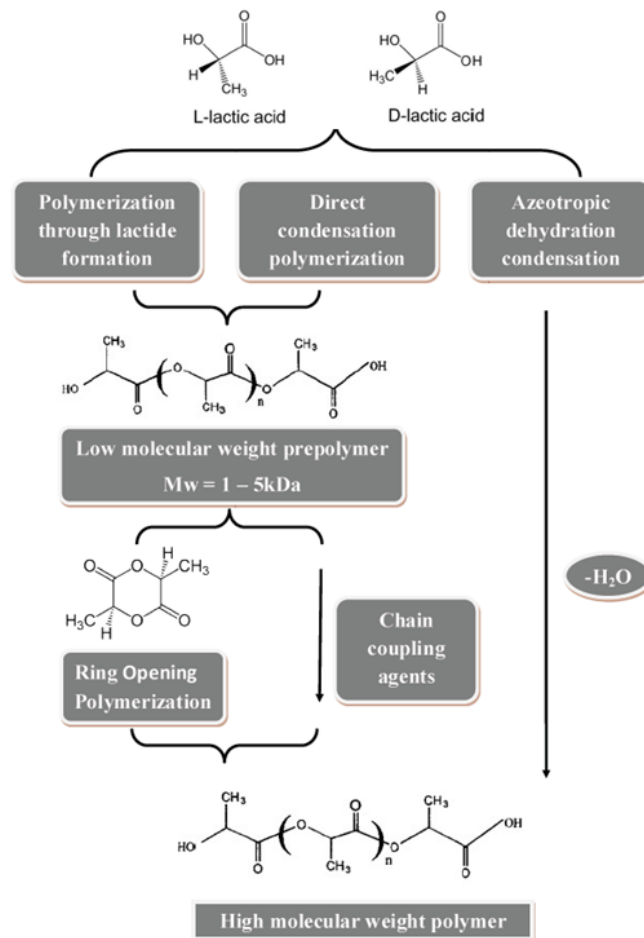


Figure 4. The manufacturing process to produce high molecular weight PLA, from [18].

ROP is the most used technique on the industrial scale due to its benefits, which include light process conditions, shorter residence durations, the absence of side products, and high molecular weights. The most common catalyst is 2-ethylhexanoic tin(II) salt, also known as stannous octoate [Sn(Oct)₂], which is authorized by the USFDA, and is typically used in conjunction with alcohol as a cocatalyst. Since impurities have a negative impact on material qualities due to the reaction's sensitivity to residual non-cyclic monomers, the real bottleneck of ROP is the availability of cyclic monomers, as well as their optical and chemical purity. Figure 5 illustrates the three stereo-isomeric forms of cyclic dimer lactide, the cyclic raw material for PLA.

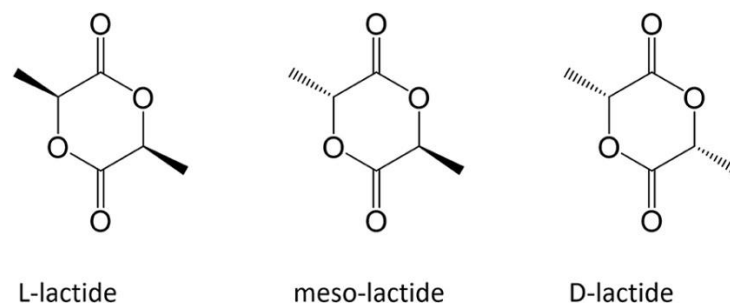


Figure 5. Cyclic dimers for ROP process.

The amount of L- and D-lactide used to create PLA depends on the procedure. Water, meso-lactide, contaminants, LA, and LA oligomers are all products of the lactide reactor [207]. It is necessary to purify the mixture, in this case by vacuum distillation via a set of columns. The highest Mw PLA is formed from L-lactide plus a tiny quantity of meso-lactide, due to the difference in the boiling temperatures of lactide and meso-lactide. The stereochemical purity of the PLA increases with the lactide mixture's stereochemical purity. Because a significant quantity of meso-lactide is produced during this process, the qualities of the PLA resin that is produced can vary depending on the amount of meso-lactide in the mixture. PLA that includes a significant amount (93%) of L-LA crystallizes.

Meso-lactide content in PLA monomers should ideally be as low as possible. Nature-Works LLC has made it feasible to refine meso-lactide into different functionalities, despite the fact that its manufacture is undesired and frequently accompanied by contaminants. The meso-lactide byproduct is used in a variety of surfactants, coatings, and copolymers as chemical intermediates [208]. The manufacture of lactide and PLA with cheap manufacturing and production costs, as well as improved characteristics, has also been the subject of extensive investigation [209]. To obtain high Mw and high optical purity, PLA has been polymerized using a variety of catalysts, including metal, cationic, and organic ones [210]. According to reports, metal complexes are one of the most effective catalysts for the ROP of the rac-lactide-based method of producing stereoblock isotactic PLA, because they can regulate factors such as molecular and chain microstructure [211].

PLA Processing

The procedures for processing PLA are tried-and-true polymer production processes utilized for other commercial polymers, including PS and PET [212]. The primary method for mass producing high Mw PLA is called melt processing, and it involves transforming the resulting PLA resin into finished goods for use in packaging [213], consumer goods, and other applications. The technique of molding molten polymers into desired shapes while they are still in a liquid state is known as melt processing. The polymer is then cooled to stabilize its final dimensions [214].

6. Discussion

It is possible to extract lignocellulosic material from cow manure, which can later be converted into glucose. This glucose can feed microorganisms that produce lactic acid, which can be polymerized into PLA. Thus, this means that it is possible to create a valuable product from waste origin. Production of bioethanol from waste manure has been studied, as has PLA production from a variety of lignocellulosic materials.

Cows are fed a high percentage of lignocellulosic fiber in their diets, and following digestion, they produce manure. Enzymatic hydrolysis into fermentable sugars could successfully disrupt the treated lignocellulosic fraction from those dejections.

Anaerobic digestion of cow manure for methane production resulted in a moderate reduction in the proportion of lignocellulosic fiber, according to research on the composition of lignocellulosic materials, in cow manure and anaerobically digested cow manure. The first step in using lignocellulosic biomass for the production of added-value products from its constituent fractions, such as hemicelluloses and cellulose, is to remove barriers that prevent chemical or biological catalysts from aiding in its transformation. Size reduction and steam explosion are examples of physical pretreatments, whereas solvents that promote cellulose, hemicellulose, and lignin degradation are used in chemical pretreatments to change the structure of biomass. The partition of cellulose into glucose units and of the hemicellulosic biomass into its constituent sugars are necessary for the conversion of lignocellulosic biomass into value-added goods. Two main approaches have been developed: acid and enzymatic hydrolysis. Enzymatic hydrolysis is the biotechnological process, while acid hydrolysis is the chemical path.

On agricultural waste, byproducts, and residues, LA can be synthesized biotechnologically and used to create biodegradable, biocompatible LA polymers. The majority of

lactic acid that is commercially generated around the world is created through the fermentation of carbohydrates by homolactic organisms from the genus *Lactobacillus*, which only produce lactic acid. By combining the enzymatic hydrolysis of carbohydrate substrates and microbial fermentation of the resulting sugars into a single phase, the bioconversion of carbohydrate materials to lactic acid can be made considerably more effectively (SSAF process).

To achieve the LA product, purification is needed after fermentation. Separation and the final purification process incur almost 50% of the production costs. Due to water's high affinity, breakdown at high temperatures, and significant energy consumption, obtaining high purity LA is problematic. Variable molecular weight PLA can be produced using LA, but typically only high Mw PLA has significant economic use in the fiber, textile, plastics, and packaging industries. The indirect way of obtaining PLA from ROP is the most widely employed approach.

Although PLA degradation has been studied for a while, knowledge of the underlying mechanisms is still lacking. Methods for the chemical recycling of these materials, together with the obtained chemical products, have been reviewed [215]. According to several studies, PLA breakdown only happens by hydrolysis and does not require any enzyme activity [216]. According to some reports, enzymes play a crucial part in the breakdown of PLA [217].

7. Conclusions

There is concern about the impact of cow manure waste and fossil-based plastic accumulation. Cow manure decomposition leads to gases such as methane and nitrogen oxide, both of these being greenhouse emissions that have an impact on the environment. Combining both problems, it is possible to manufacture a value-added product such as PLA from cow manure, and thus solve emission problems.

Lignocellulosic biomass contains a variety of minor sugars in addition to xylose and glucose. From an economic standpoint, it is highly beneficial if all sugar substrates are utilized. Hexoses' and pentoses' transformation ratios from lignocellulosic fraction into LA would have an important impact on process viability.

It is possible to extract the lignocellulosic fraction from cow manure and convert it into glucose. This glucose can be used to feed the microorganisms that produce LA. The obtained lactic acid can be polymerized, achieving the final product: PLA. The obtained PLA would be a replacement for petro-chemical polymers due to its biodegradability properties, improving the environmental problems.

Existing pretreatments are not adequate, and existing nonthermal advances combined with organic mild chemical process are likely to increase the conversion yields' released inhibitory compounds potential. It is fundamental to enhance LA generation without sacrificing the optical quality or adding extra costs into LA polymers. Cow manure is a possible source for PLA production.

The separation and purification processes are critical for LA production viability: 50% of the costs are incurred by these processes, and they have many drawbacks, such as water affinity, decomposition at high temperatures, and elevated energy consumption.

As a result of the review, to obtain PLA from cow manure, the required technological sequence consists of manure treatment, pretreatment to prepare for hydrolysis process, saccharification, and fermentation. Pretreatment may be performed with a diluted acid treatment if lignin content is low enough. Saccharification and fermentation could be carried out together or separately, depending on the microorganism, affecting the degradation of hexoses and pentoses. After the LA process, the sequence is similar to current industrial processes, but it is necessary to consider the effect of the substrate on the purification, polymerization, and final product characteristics. Further research is needed to validate the entire process yield, as well as the properties of the obtained PLA.

Author Contributions: Conceptualization, L.F.C., R.G. and V.F.; methodology, L.F.C. and V.F.; investigation, R.G. and O.P.N.; resources, L.F.C.; data curation, L.F.C.; writing—original draft preparation, R.G.; writing—review and editing, L.F.C., O.P.N. and V.F.; visualization, R.G.; supervision, L.F.C. and V.F.; project administration, L.F.C.; funding acquisition, L.F.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work has received financial support from the Doctorat Industrial grant (2021 DI 22) from the AGAUR through the Secretariat of Universities and Research of the Department of Business and Knowledge of the Generalitat de Catalunya. This work is partially supported by ICREA under the ICREA Academia programme.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are available upon request to the corresponding author.

Acknowledgments: The authors at the University of Lleida would like to thank the Catalan Government for the quality accreditation given to their research group GREiA (2017 SGR 1537). GREiA is a certified agent TECNIO in the category of technology developers from the Government of Catalonia.

Conflicts of Interest: The authors declare no conflict of interest.

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